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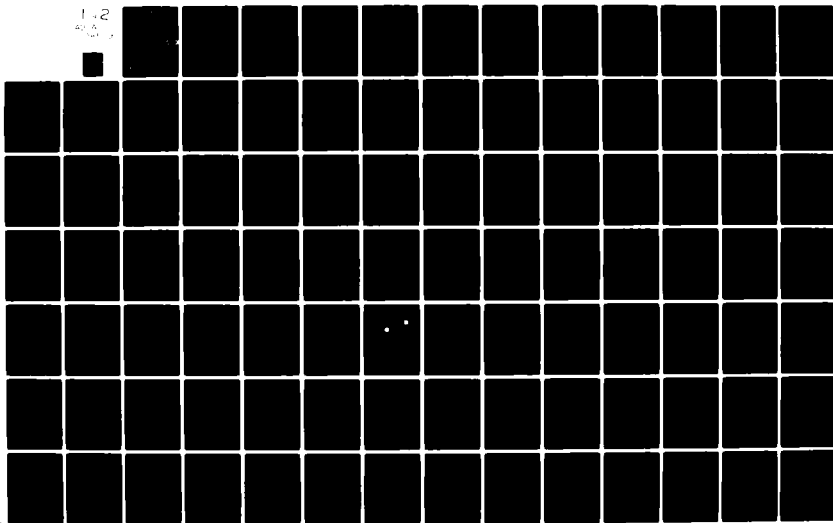
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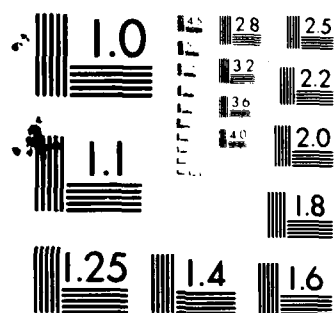
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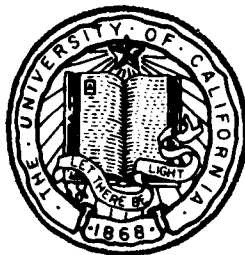
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San Diego, California 92152

**DIFFERENTIAL SOUND ABSORPTION TECHNIQUE  
AND  
EFFECT OF ION-PAIRING AND PRESSURE ON SOUND ABSORPTION  
IN SEAWATER AND  
AQUEOUS MIXTURES OF MAGNESIUM SULFATE AND SODIUM CHLORIDE**

Cheng-Chih (Paul) Hsu

Sponsored by  
Office of Naval Research, Code 480 Acoustics  
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NSF OCE78-25123  
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UNIVERSITY OF CALIFORNIA, SAN DIEGO  
MARINE PHYSICAL LABORATORY OF THE  
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SAN DIEGO, CALIFORNIA 92152

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*Kenneth M. Watson*

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Sound absorption in the ocean between 5 kHz and 350 kHz is principally due to the relaxation process associated with a pressure dependent chemical reaction of $MgSO_4$ . This research has resolved two conflicts regarding (1) the effect of pressure on sound absorption and relaxation frequency due to $MgSO_4$ in sea water and (2) the reduction of sound absorption by the addition of up to 0.6 M NaCl to low concentration (0.02M) solution of NaCl. <i>2005/10/18</i>		

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At 25° the decrease in absorption from the pressure measurements to 307 ATM for Lyman and Fleming seawater (3070 m depths) yielded a pressure coefficient of  $8.1 \times 10^{-4} \text{ ATM}^{-1}$  compared to the value of  $6.46 \times 10^{-4} \text{ ATM}^{-1}$  from Schulkin and Marsh or  $12.7 \times 10^{-4} \text{ ATM}^{-1}$  from Bezdek. Contrary to the increase in relaxation frequency with increasing depth reported by Bezdek, the relaxation frequency remained constant at  $139 \pm 4 \text{ kHz}$ . Additional pressure measurements on  $0.02 \text{ MgSO}_4$  and  $0.02 \text{M MgSO}_4 + 0.6 \text{M NaCl}$  solutions yielded a pressure coefficient of  $6.4 \times 10^{-4} \text{ ATM}^{-1}$ .

The reduction of absorption in  $\text{MgSO}_4$  solution upon the addition of NaCl can be accounted for theoretically by Debye-Huckel theory and by formation of  $\text{MgCl}^+$  and  $\text{NaSO}_4^-$  ion-pairs. The measured reduction is less than that observed by Kurtze and Tamm, however. At this concentration of  $\text{MgSO}_4$ , the effects of ionic strength and ion-pairing are about equal. The results are consistent with dissociation constants of 0.0062, 0.1, 0.178 for the  $\text{MgSO}_4$ ,  $\text{NaSO}_4^-$  and  $\text{MgCl}^+$  ion-pairs, respectively up to 0.12 M NaCl addition. For 0.6M NaCl addition to 0.02 M  $\text{MgSO}_4$ , the absorption results cannot be explained by either simple Debye-Huckel theory, the Johnson and Pytkowicz model of ion-pairing nor the Pitzer approach.

The values of maximum absorption per wavelength were determined to an absolute accuracy of about 1% from  $80 \times 10^{-6}$  to  $16 \times 10^{-6}$ . For the differential absorption measurements in  $\text{MgSO}_4$  and NaCl mixtures, the measurement accuracy is sufficient for quantitative studies of ion pairing in electrolyte mixtures, particularly for unsymmetrical salts.

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## LIST OF SYMBOLS

$A$	Constant in the Debye-Hückel activity coefficient equation. $A = .5115$ at $25^\circ\text{C}$ .  Constant in the Schulkin and Marsh equation. $A = 2.34 \times 10^{-6}$ .
$a$	Degree of dissociation of magnesium sulfate.
$a_1$	Coefficient in Eq. (VI.1).
$a_2$	Coefficient in Eq. (VI.1).
$B$	Constant in the Debye-Hückel activity coefficient equation. $B = .3291 \times 10^8$ at $25^\circ\text{C}$ .
$b$	Pressure factor for a linear dependence on pressure.
$b_1$	Pressure factor dependent on $P$ for a polynomial dependence on pressure.
$b_2$	Pressure factor dependent on $P^2$ for a polynomial dependence on pressure.
$C$	Sound speed.
$C_i$	Charged species in solution.
$d$	Distance parameter.
$d_1$	Decay rate of sound wave in test solution.
$d_2$	Decay rate of sound wave in background solution.
$F$	$F$ -number defined by Eqs. (IV.7) and (IV.8).
$f$	$f$ -number in the Kurtze and Tamm's empirical equation.  Frequency.
$f_1$	Activity coefficient of $\text{MgSO}_4$ .
$f_{\pm MN}$	Free mean activity coefficient of $MN$ , $MN = \text{MgSO}_4$ , $\text{NaSO}_4^-$ or $\text{MgCl}^+$ .
$f_{\text{SO}_4^{--}}$	Free activity coefficient of ion $\text{SO}_4^{--}$ .
$f_{\text{Mg}^{++}}$	Free activity coefficient of ion $\text{Mg}^{++}$ .

$f_{MN}$	Activity coefficient of ion-pair $MN$ .
$f_r$	Relaxation frequency.
$f_{r_i}$	Relaxation frequency of the $i$ -th relaxation process.
$I$	Ionic strength defined by Eq. (IV.14).
$K$	Thermodynamic dissociation constant of magnesium sulfate.
$K^*$	Stoichiometric association constant.
$K_m$	Conventional equilibrium constant.
$K_{ij}$	Equilibrium constant in the 4-state model.
$k_{ij}$	Reaction rate in the 4-state model.
$k_{12}^?$	Defined by Eq. (A.10).
$k'_{12}$	Defined by Eq. (A.10).
$k'_{23}$	Defined by Eq. (A.9).
$L$	Number of molecules per mole.
$M$	Mole/liter.
$m_i$	Concentration of the species in the 4-state model.
$n$	Concentration in moles per unit volume.
$P$	Pressure.
$Q$	Quality factor.
	Sound absorption cross-section.
$R$	Gas constant, $82.057 \text{ cm}^3 \text{ atm/mole } ^\circ\text{K}$ .
$S$	Salinity.
$T$	Temperature.
$v$	Sound speed.
$V_i$	Partial volume of the species in the 4-state model.
$W$	Work.
$Z_i$	Charge valence of the species in solution.
$\alpha$	Absorption constant of sound wave.



$\beta$	Isothermal compressibility.
$\beta_s$	Adiabatic compressibility.
$\beta_o$	Static compressibility.
$\beta'_o$	Chemical compressibility.
$\beta_r$	Relaxational compressibility.
$\beta_{III}$	Chemical compressibility defined by Eq. (A.12).
$\gamma_{\pm}$	Stoichiometric mean activity coefficient of magnesium sulfate.
$\lambda$	Wavelength of sound wave.
$\omega$	Angular frequency.
$\kappa$	Angular relaxation frequency.
$\kappa_{III}$	Angular relaxation frequency defined by Eq. (A.8).
$\tau$	Time constant of the relaxation process.
$\rho$	Density.
$\eta$	Viscosity.
$\eta_w$	Viscosity of water at 25 °C and 1 atm.
$\sigma$	Standard deviation.
$\sigma_o$	Minimum standard deviation.
$\pi'$	Ratio of the mean activity coefficient square to the activity coefficient of ion-pair.
[ ]	Concentration.
[ ] <sub>T</sub>	Total concentration of the ion.
$(\alpha\lambda)_m$	Maximum absorption per wavelength.

## ACKNOWLEDGMENT

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## PREFACE

Kurtze and Tamm found that excess sound absorption in aqueous magnesium sulfate solutions decreases with the addition of sodium chloride. According to their results the ratio of the decrease in sound absorption (from that in pure magnesium sulfate solution) to the sound absorption in mixture was shown to be linearly proportional to the ratio of the formal concentration of sodium chloride to that of magnesium sulfate. Kurtze and Tamm claimed that the constant of proportionality for such measurements was independent of the formal concentration of magnesium sulfate. The initial measurements of this study showed that Kurtze and Tamm's data relating to low concentration solutions are in error.

The addition of sodium chloride causes a decrease in the concentration of magnesium sulfate ion-pairs in favor of the formation of sodium sulfate ion-pairs and magnesium chloride ion-pairs. The earlier acoustic results pertaining magnesium sulfate, sodium chloride, sodium sulfate, and magnesium chloride solutions showed that in the frequency region of 100 KHz, only magnesium sulfate solutions exhibit significant excess sound absorption. Thus, either in the pure magnesium sulfate solutions or in the magnesium sulfate and sodium chloride mixtures sound absorption may be attributed only to the magnesium sulfate in the solutions. Further examinations of the sound absorption theory found that the sound absorption in these solutions is approximately proportional to the magnesium sulfate ion-pairs concentration if the addition of sodium chloride does not significantly affect the physical properties of the solution. Hence, sound absorption data may be used to measure the magnesium sulfate ion-pair concentration and thus to provide a quantitative basis for analyzing ion-pairing in the solution. Earlier attempts to interpret the results quantitatively were not successful. In this study, an initial theoretical analysis based on modern electrolyte theory found that the differential sound absorption in the magnesium sulfate-sodium chloride system may also be dependent on the formal concentration of magnesium sulfate since the constant of proportionality, as observed by Kurtze and Tamm, may not be a single constant of 0.21. It also showed that the results can be

interpreted on the basis of the ion-pairing and the ionic strength effect.

In studies of conductance measurements for weakly associated unsymmetrical electrolyte solutions, good fits of conductance data to conductance equations could be obtained for a wide range of distance parameters. Fisher and Fox in their conductance measurements observed variations of about a factor of two in dissociation constants due to the nonuniqueness of the distance parameter for sodium sulfate and magnesium chloride. The weakness of the Debye-Hückel equation of modern electrolyte theory makes its use difficult in studies of unsymmetrical electrolytes. To eliminate the ambiguities one must employ a proper basis for distance parameter determination. Fisher and Fox introduced the use of Kurtze and Tamm's differential sound absorption data and showed that it is useful in choosing a proper distance parameter. However, they pointed out that further examination of the differential sound absorption in magnesium sulfate solutions may be necessary for improved results. In their conductance measurements for alkali-sulfates, discrepancies on dissociation constants were found between their results and those of others with Fisher and Fox arguing for higher association by about a factor of two. An extended differential sound absorption study was suggested to check on the conductance results for those unsymmetrical electrolyte solutions.

Sound absorption measurements can be made to furnish more differential sound absorption data for the magnesium sulfate-sodium chloride system. The differential sound absorption technique would be expected to act as an independent means of studying the roles of sodium sulfate and magnesium chloride ion-pairs in the magnesium sulfate-sodium chloride system and as a model for investigating other unsymmetrical ion-pairing in other magnesium sulfate-alkali chloride systems. These studies comprise the major subject of this research. Pressure measurements would further extend the range of application of the differential sound absorption technique. Studies covering magnesium sulfate solutions and magnesium sulfate-sodium chloride mixtures would provide the basis for understanding ion-pairing and ion-speciations in seawater.

Sound absorption between 30 to 300 KHz in seawater is dominated by the magnesium sulfate relaxation. The pressure effect on sound absorption in seawater thus far relies on the data from Fisher's measurements made for .5M magnesium sulfate solution and Bezdek's *in situ* measurements in the Pacific Ocean. Although the magnitude of sound absorption was found to decrease with increased pressure in both magnesium sulfate solutions and seawater, a quantitative agreement has not been reached. Fisher found no appreciable shift of relaxation frequency with a pressure increase in .5M magnesium sulfate solution while Bezdek observed an increase in the relaxation frequency as the depth increased in seawater. Sound absorption measurements found that the relaxation frequency decreases with the decrease of temperature in both magnesium sulfate solutions and seawater. This situation calls for more studies relating to not only sound absorption in seawater itself but also the effect on sound absorption due to the presence of other salts in seawater. The whole issue necessitates an understanding of the interactions and the structures of the major species in seawater. Therefore, seawater measurements are included in this research so that a complete study centered on sound absorption associated with the relaxation process of magnesium sulfate may be obtained.

Differential Sound Absorption Technique  
and  
Effect of Ion-pairing and Pressure on Sound Absorption  
in Seawater and  
Aqueous Mixtures of Magnesium Sulfate and Sodium Chloride

by

Cheng-chih ( Paul ) Hsu

Doctor of Philosophy in Electrical Engineering (Applied Ocean Science)

University of California, San Diego, 1981

Professor Victor C. Anderson, Chairman

Doctor Frederick H. Fisher, Co-Chairman

Sound absorption in magnesium sulfate solutions was found to decrease with the addition of sodium chloride. The initial measurement results of Kurtze and Tamm showed that the ratio of the reduction in sound absorption to the new absorption in solution is linearly proportional to the ratio of the concentration of sodium chloride to that of magnesium sulfate. Earlier attempts at interpretation ended with only a qualitative agreement concerning the measurement results. Recently, a theoretical study of the magnesium sulfate and sodium chloride system found that the initial result may not be valid for solutions of low magnesium sulfate concentration. Further measurements for these solutions would help to clarify this problem.

An extensive differential sound absorption technique was studied for the magnesium sulfate-sodium chloride system. Assuming a linear dependence of sound absorption upon

magnesium sulfate ion-pair concentration in .02M magnesium sulfate solution and its mixtures with sodium chloride, a theoretical method of estimation was devised for analyzing the differential magnesium sulfate ion-pair concentration and the differential sound absorption which occurred after the addition of sodium chloride. The association characteristics of the ions in the solution can then be checked with the results from the sound absorption measurements. Other unsymmetrical alkali sulfate ion-pairs can also be checked in a similar fashion. Discrepancies in the dissociation constants for the unsymmetrical alkali sulfate ion-pairs continue to exist.

Few works on relaxational excess absorption in seawater exist, particularly on the pressure effect on sound absorption. Sound absorption in seawater is dominated by the magnesium sulfate equilibrium. Earlier investigations have not agreed on the effect which the pressure has on the magnitude of sound absorption. For magnesium sulfate solutions, no appreciable shift of relaxation frequency was found for pressure changes. The *in situ* measurements in the sea showed increases in relaxation frequency with depth.

For the following solutions sound absorption measurements using the titanium spherical resonator method were made in the region of 30 to 300 KHz at 25 °C and pressures up to 307 atm: water, .03M sodium sulfate solution, sodium chloride solutions of .16M and .58M, .02M magnesium sulfate solution, mixtures of .02M magnesium sulfate and .02, .04, .08, .12, .6M sodium chloride, and Lyman and Fleming seawater. Excess sound absorption of these sodium chloride and sodium sulfate solutions was not detected. Excess relaxational sound absorption was then analyzed for magnesium sulfate solution, magnesium sulfate and sodium chloride mixtures and seawater.

The pressure measurements for these solutions showed no significant shift in relaxation frequency when the pressure increase was from 1 to 307 atm. Assuming a linear dependence of sound absorption in this pressure range, the pressure factors obtained were:  $6.4 \times 10^{-4}$  atm $g^{-1}$  for .02M magnesium sulfate solution,  $6.5 \times 10^{-4}$  atm $g^{-1}$  for .02M magnesium sulfate and

.6M sodium chloride mixture, and  $8.1 \times 10^{-4}$  atm $g^{-1}$  for seawater. According to the results for pure magnesium sulfate solution and seawater, calculations based on the electrolyte theory showed that in seawater 9.0-10.3 % of the total magnesium ions are paired to sulfate ions and 17.1-19.5 % of the total sulfate ions are paired to magnesium ions.

The results from the measurements taken during this study support the theoretical method of estimation for the magnesium sulfate-sodium chloride system. This investigation showed that the differential sound absorption technique provides an independent method to quantitatively study the ion-pairing in the magnesium sulfate-sodium chloride system. This technique can be extended to other magnesium sulfate-alkali chloride systems. With further improvements in this technique it may prove useful in dealing with solutions of high sodium chloride content and seawater as well.



## I. BACKGROUND STATEMENT

Magnesium sulfate solutions exhibit excess sound absorption in addition to the classical absorption which is due to the viscosity and thermal conductivity of the solution.<sup>1-3</sup> The excess absorption is attributed to the pressure-dependent relaxation process associated with the acoustic perturbation of the magnesium sulfate equilibrium.<sup>1</sup> The excess sound absorption associated with the chemical equilibrium of magnesium sulfate is principally explained by the complex dynamic chemical compressibility. The contribution from the specific heat was shown to be trivial.<sup>1</sup> The partial volumes occupied by ions and ion-pairs in the aqueous solution are different. Thus, according to the Le Chatelier's principle, volume changes, in addition to the usual changes of the bulk volume of the solution, occurred as a result of the pressure variations caused by the sound wave. The partial volume change is related to the equilibrium constant by van't Hoff equation. It introduces a frequency-dependent complex term in the compressibility of the solution and, thus, causes excess sound absorption.

Since the volume change does not always follow the variation of the pressure, the work done by the sound wave in the compression cycle which is expressed by

$$W = - \int P dV \quad (1.1)$$

where  $P$  is the pressure and  $V$  is the volume, can not be restored from the solution during the expansion cycle. Thus, a net loss exists in each complete cycle of sound wave propagation in the solution. For a finite period of time, there will be an accumulated energy loss which appears as a reduction of the pressure amplitude of sound wave.

Several different reasons could be advanced for this hypothesis. When the phase difference between the pressure and volume is zero, no delay of the volume change occurs following the variation of the pressure and the absorption of acoustic energy is zero. However, in most of the cases, the phase delay is not negligible and the absorption is significant. The frequency of the sound wave plays an important role in sound absorption. At relatively low fre-

quencies, the loss of the energy during the compression cycle can be almost totally regained from the solution and nearly no net absorption results. On the other hand, however, at relatively high frequencies, the change in the volume is very slow compared to the rapid change in the pressure. Therefore, the whole system seems not to be affected by the sound wave and again no sound absorption results. For other frequencies, there are phase differences and, hence, sound absorption resulted. It is only at the frequency where the greatest phase delay takes place that the maximum sound absorption occurs.

Consider a 2-state chemical equilibrium in the magnesium sulfate solution,



This equilibrium is determined by factors such as pressure, temperature, concentration etc.. When a change in these factors occurs, the equilibrium has to adjust itself to a new state. The shift in the chemical equilibrium with the change of pressure may be explained by the Le Chatelier's principle. Due to the shift in the chemical equilibrium the concentrations of the species in the solution and the volume of the solution are affected. Thus, two kinds of pressure-induced volume changes result. One is due to the static compressibility of the solution and the other is due to the shift in the chemical equilibrium (or the chemical compressibility). The former is usually much bigger than the latter and is always in phase with the pressure change. The latter is basically a relaxation process determined by the characteristics of the solution. A phase delay of the volume change with respect to the pressure change always occurs in this case and an acoustic energy loss (or excess sound absorption) is then introduced.

Let  $m$  be the formal concentration of the solution, then the concentration of the magnesium sulfate ion-pair is  $m(1-a)$  and that of the magnesium ion or the sulfate ion is  $ma$ , where  $a$  is the degree of dissociation of the magnesium sulfate. The total volume of the solution can be expressed by

$$V = n_1 V_1 + n_2 V_2 + n_3 V_3 + n_w V_w \quad (1.3)$$

where  $n_{i,i=1,2,3,w}$  is the total number of mole of the magnesium sulfate ion-pair, of the magnesium ion, of the sulfate ion and water, respectively. Similarly,  $V_i$  is the partial molar volume of the corresponding species in the solution. Since  $n_1 = Vm(1-a)$  and  $n_2 = n_3 = Vma$ , differentiating Eq. (1.3) gives

$$\begin{aligned} \frac{\partial V}{\partial a} &= \frac{\partial n_1}{\partial a} V_1 + \frac{\partial n_2}{\partial a} V_2 + \frac{\partial n_3}{\partial a} V_3 + \frac{\partial n_w}{\partial a} V_w \\ &= Vm(-V_1 + V_2 + V_3) \\ &= Vm(\Delta V^0) \end{aligned} \quad (1.4)$$

where  $\Delta V^0 = V_2 + V_3 - V_1$ . The dissociation constant  $K$  is expressed by

$$K = \frac{m^2 a^2 f_{\pm}^2}{m(1-a)f_1} \quad (1.5)$$

where  $f_{\pm} = (f_{Mg^{++}} f_{SO_4^{--}})^{1/2}$  is the mean activity coefficient of magnesium sulfate and  $f_1$  is the activity coefficient of the magnesium sulfate ion-pairs. Differentiating Eq. (1.5) with respect to pressure,  $P$ , then,

$$\frac{\partial K}{\partial P} = K \left( \frac{2-a}{a(1-a)} + \frac{2}{f_{\pm}} \frac{\partial f_{\pm}}{\partial a} - \frac{1}{f_1} \frac{\partial f_1}{\partial a} \right) \frac{\partial a}{\partial P} \quad (1.6)$$

Also, by van't Hoff equation, one has

$$\frac{\partial K}{\partial P} = - \frac{K(\Delta V^0)}{RT} \quad (1.7)$$

Then, using Eqs. (1.4), (1.6) and (1.7) the chemical compressibility would be

$$\begin{aligned} \beta'_0 &= - \frac{1}{V} \frac{\partial V}{\partial P} \\ &= - \frac{1}{V} \frac{\partial V}{\partial a} \frac{\partial a}{\partial P} \\ &= - \frac{m(\Delta V^0)^2}{RT} \left( \frac{2-a}{a(1-a)} + \frac{2}{f_{\pm}} \frac{\partial f_{\pm}}{\partial a} - \frac{1}{f_1} \frac{\partial f_1}{\partial a} \right)^{-1} \end{aligned} \quad (1.8)$$

Since the change of the activity coefficient with respect to the degree of dissociation is ganerally

negligible, only the first term inside the bracket of Eq. (I.8) is significant. Thus,

$$\beta'_0 = \frac{ma(1-a)}{2-a} \frac{(\Delta V^0)^2}{RT} \quad (I.9)$$

Considering the pressure-induced perturbation on the chemical equilibrium, the reaction rate equation of the equilibrium in Eq. (I.2) may be written as

$$\frac{d(m(1-a))}{dt} = - \frac{d(ma)}{dt} = k_2 \pi^f (ma)(ma) - k_1 m(1-a) \quad (I.10)$$

where  $\pi^f = f_{\pm}^2/f_1$ . Assuming  $\Delta a \ll a$  and  $(\Delta a)^2 \approx 0$  and including the perturbation terms  $\Delta a$  and  $\Delta \pi^f$ , Eq. (I.10) can be simplified to

$$\tau \frac{d(\Delta a)}{dt} + \Delta a = 0 \quad (I.11)$$

where  $\tau = (k_1 + k_2 ma \pi^f (2 + \frac{a}{\pi^f} \frac{\partial \pi^f}{\partial a}))^{-1}$  is the time constant of this relaxation process.

The solution of Eq. (I.11) is

$$\Delta a = (\Delta a)_0 e^{-t/\tau} \quad (I.12)$$

where  $(\Delta a)_0$  is the initial value of the perturbation. For a perturbation which follows a sinusoidal variation of the form  $Ue^{i\omega t}$ , Eq. (I.11) becomes

$$\tau \frac{d(\Delta a)}{dt} + \Delta a = (\Delta a)_0 e^{i\omega t} \quad (I.13)$$

The solution of this equation is

$$\Delta a = \frac{(\Delta a)_0}{1 + i\omega\tau} \quad (I.14)$$

Hence, for a sinusoidal driving pressure, the relaxational compressibility,  $\beta_r$ , for the chemical equilibrium of Eq. (I.2) can be related to the chemical compressibility,  $\beta'_0$ , by

$$\beta_r = \frac{\beta'_0}{1 + i\omega\tau} \quad (I.15)$$

The total compressibility may be considered to consist of two terms such that

$$\beta_t = (\beta_0 - \beta'_0) + \beta_r \quad (I.16)$$

where  $\beta_0$  is the static compressibility. In a media with acoustic energy loss, the sound wave is expressed by

$$P = P_0 e^{i\omega(t - x/v)} \quad (1.17)$$

where  $P_0$  is the initial pressure amplitude and

$$\frac{1}{v} = \frac{1}{C} - i\frac{\alpha}{\omega} \quad (1.18)$$

where  $\alpha$  is the absorption constant. Using the relation of

$$\frac{1}{v^2} = \beta_s \rho \quad (1.19)$$

where  $\rho$  is the density of the solution, and substituting Eqs. (1.16) and (1.18) into Eq. (1.19) and equating the imaginary parts, the following result can be obtained.

$$2\alpha = \frac{\omega^2 C \tau \beta'_0 \rho}{1 + \omega^2 \tau^2} \quad (1.20)$$

Since in most of the cases  $\beta_0 \rho \approx 1/C^2$ , this result can be further written as

$$\alpha = \frac{\pi \omega \tau \beta'_0}{\lambda \beta_0 (1 + \omega^2 \tau^2)} \quad (1.21)$$

The absorption per wavelength is then

$$\alpha \lambda = \frac{\beta'_0}{\beta_0} \frac{\pi \omega \tau}{1 + \omega^2 \tau^2} \quad (1.22)$$

The maximum absorption per wavelength would be

$$(\alpha \lambda)_m = \frac{\pi}{2} \frac{\beta'_0}{\beta_0} \quad (1.23)$$

or

$$(\alpha \lambda)_m = \frac{\pi}{2} \frac{(\Delta V^0)^2}{\beta_0 R T} \frac{ma(1-a)}{2-a} \quad (1.24)$$

Sound absorption measurements of this study were made by the spherical resonator method which has been used successfully for solutions.<sup>3,76,99,115-117</sup> This method uses a sphere as a solution container in which sound waves are excited in resonant modes. The raw data

measured are decay rates of the pressure amplitude of sound wave, from which sound absorption data are obtained. Sound signals are transmitted and received at the outer wall of the sphere. Hence, the measured sound absorption represents the sum of the sound absorptions due to both the solution and the sphere. That due to the sphere presumably remains constant for different solutions. The classical sound absorption in solution A is assumed to be the sound absorption in solution B, which shows no excess sound absorption and has similar viscosity and thermal conductivity properties as solution A. Thus, subtracting the absorption measured from solution B from that of solution A, the residue would be the excess sound absorption in solution A. A description of the measuring technique is given in Chapter II.

For magnesium sulfate solutions the excess sound absorption can be solely attributed to the magnesium sulfate equilibrium. After the addition of sodium chloride, not only may additional excess absorption be introduced<sup>3,6-9</sup> but the classical sound absorption may be altered.<sup>89-91</sup> The assessment of the excess absorption<sup>77</sup> depends on the assessment of the classical absorption. A similar consideration is required for seawater measurements as well as for the measurements at elevated pressures. An examination of this concern is provided in Chapter III.

Excess sound absorption in solutions can be conceptually explained with a 2-state association model for the equilibrium.<sup>1</sup> Sound absorption theory based on the 2-state association model has been shown to qualitatively explain the primary excess sound absorption for magnesium sulfate solutions.<sup>1-4,115,116,119,129</sup> However, this theory fails to explain the other relaxational sound absorptions for magnesium sulfate solutions. It was found<sup>3,64,66</sup> that magnesium sulfate solutions show a primary relaxational excess sound absorption in the 100 KHz region, a second one in the 200 MHz region and, likely, a third one in the 10 MHz region. Only the primary relaxational sound absorption is investigated in this study. The observation of multiple relaxational sound absorptions was later explained by the theory devised by Eigen and Tamm<sup>10</sup> on the basis of a 4-state association model for the magnesium sulfate equilibrium, in which

three species of neutral ion-pairs were assumed to be involved in various degrees of hydration and the primary excess sound absorption was attributed to the equilibrium where the last water molecule of the hydrated ion-pair was repelled. A brief summary of this theory is given in the Appendix A. This theory as well as the 4-state association model have been widely applied<sup>17,62-75</sup> and tested. Fisher<sup>73,74</sup> found that for .5M magnesium sulfate solution for a 1000 atm pressure increase there is a 60 % reduction in sound absorption and only a 10 % decrease in  $MgSO_4$  concentration and that this observation can only be explained by Eigen and Tamm's<sup>10</sup> 4-state theory. However, disagreement concerning the dynamic parameters for the theory<sup>17,62-65,68</sup> continues to exist. This disagreement should be resolved in such a way that a completely quantitative model for interpretation of the acoustic data would be obtained.

The effect on the primary sound absorption in magnesium sulfate solutions due to the addition of other salts has been investigated by Kurtze and Tamm.<sup>3</sup> This initial study found that the addition of sodium chloride causes reduction in sound absorption. According to Kurtze and Tamm<sup>3</sup> this reduction in absorption was expressed empirically by an equation of  $\Delta\alpha/\alpha = f[NaCl]/[MgSO_4]$ , where  $\Delta\alpha = \alpha_0 - \alpha$ ,  $\alpha_0$  is the absorption constant of the original magnesium sulfate solution,  $\alpha$  is that after the addition of sodium chloride,  $f$  is a constant of .21 for magnesium sulfate solutions and [ ] denotes the formal concentration of the salt. Earlier studies<sup>4,102</sup> seeking a quantitative explanation of this reduction of sound absorption were not successful. A theoretical study recently made by Neuberger, Hsu and Fisher<sup>5</sup> for the same purpose found that the  $F$ -number ( $F$  is used hereafter to substitute for the  $f$  used by Kurtze and Tamm) is not a constant, but is a function dependent on the magnesium sulfate concentration. This result is in conflict with that of Kurtze and Tamm. Thus, further studies appeared necessary to resolve the discrepancy. For this purpose additional measurements were made in this study. The measurements, results and discussions are given in Chapter IV.

In modern electrolyte theory, the Debye-Hückel equation for calculating the activity coefficients of ions is less valid for unsymmetrical salts than for symmetrical salts due to the

linearization of the Boltzmann distribution law.<sup>12,13</sup> Therefore, results from studies of unsymmetrical salts based on the Debye-Hückel equation are, in general, less convincing than those of symmetrical salts. The Debye-Hückel equation, after being improved by considering the short-range ion-ion interactions, is believed to be in general valid for uni-univalent electrolyte solutions of concentrations up to .1M.<sup>12-14</sup> Further improvement was made on the Debye-Hückel equation by adding extra ionic strength dependent terms.<sup>13-15</sup> This treatment is empirical and its concept is not generally accepted. Agreement in determining the distance parameter and the ionic strength dependence has not been obtained. The addition of sodium chloride to magnesium sulfate solutions is assumed to give rise to equilibria associated with  $\text{NaSO}_4^-$ ,<sup>16,30-35</sup>  $\text{MgCl}^+$ <sup>15,36</sup> and  $\text{NaCl}^0$ <sup>37-46</sup> ion-pairs, aside from the one with  $\text{MgSO}_4^0$ <sup>17-30</sup>, which has been in the solution before the addition of sodium chloride. Thus, after the addition of sodium chloride the  $\text{MgSO}_4^0$  ion-pair concentration would be reduced in favor of the formations of  $\text{NaSO}_4^-$  and  $\text{MgCl}^+$ . A quantitative analysis of the concentrations of the species in solutions has been discussed in the study by Neuberger, Hsu and Fisher.<sup>5</sup> This study showed that both ionic-strength and ion-pairing effects play important roles in the reduction of  $\text{MgSO}_4^0$  concentration. Sound absorption is related to  $\text{MgSO}_4^0$  concentration and is reduced with the reduction of  $\text{MgSO}_4^0$  after the addition of sodium chloride. Thus, sound absorption data could be useful in arguing the association behaviors of the unsymmetrical ion-pairs,  $\text{NaSO}_4^-$  and  $\text{MgCl}^+$ . Furthermore, the addition of other kinds of alkali-halides to magnesium sulfate solutions is presumed to follow a pattern similar to that of the addition of sodium chloride. Hence, a study of the mixture of magnesium sulfate and sodium chloride would also provide a model for investigating other unsymmetrical alkali-sulfate ion-pairs. Fisher and Fox<sup>16</sup> have pointed out the large discrepancy between their own results of the dissociation constants of  $\text{RbSO}_4^-$  and  $\text{CsSO}_4^-$  and those obtained by Reardon.<sup>33</sup> They suggested the use of the differential sound absorption technique. This technique is described in Chapter IV.

Pressure measurements are essential to understanding the partial volume information for electrolytes.<sup>11,14-17,59-61</sup> Pressure effect on sound absorption in magnesium sulfate solutions



as well as on the magnesium sulfate equilibrium has been investigated by Fisher<sup>73,104,105,119</sup> and Fisher and Fox.<sup>17</sup> These studies not only showed agreement of the partial volume data with that obtained theoretically for magnesium sulfate solution but also provided the only available pressure factor on sound absorption applicable for seawater calculations.<sup>106,109</sup> From the measurements made in the Pacific Ocean, Bezdek<sup>110</sup> found that the magnitude of sound absorption in seawater decreases while the relaxation frequency increases with depth. This observation of pressure effect on the magnitude of sound absorption is similar to that found by Fisher<sup>104,119</sup> for .5M magnesium sulfate solution, although to different extent. However, Fisher<sup>104,119</sup> found no appreciable shift of the relaxation frequency with pressure. In order to further understand the behavior of magnesium sulfate equilibrium and sound absorption in magnesium sulfate solution, magnesium sulfate and sodium chloride mixture and seawater, sound absorption measurements were made at elevated pressures. This pressure investigation is reported in Chapter V.

An examination of sound absorption in a sequence from magnesium sulfate solution, magnesium sulfate and sodium chloride mixture to seawater would represent a systematic study of the effects on both the sound absorption mechanism centered in magnesium sulfate equilibrium and the magnesium sulfate equilibrium itself.<sup>60,61</sup> In the mixture of magnesium sulfate and sodium chloride, sound absorption originates from the magnesium sulfate equilibrium and is reduced due to the addition of sodium chloride. Excess sound absorption in seawater may be considered to be based on sound absorption due to the combination of magnesium sulfate and sodium chloride. Yet, there is no complete acoustic data available for such a systematic study. Thus, additional measurements were also made for .02 M magnesium sulfate and .6M sodium chloride mixture and seawater as well. Results are given in Chapter VI.

Chemical oceanographers are concerned with ion-speciation and interactions between ions in seawater.<sup>60,61</sup> This issue has been studied in a variety of ways.<sup>42-46,50,60,61</sup> The initial use of acoustic data in this aspect of studies was made by Fisher<sup>107</sup> for magnesium and sulfate ions using acoustic data from Wilson and Leonard<sup>80</sup> and Kurtze and Tamm<sup>3</sup> and data from con-

ductance measurements. A demonstration of how the acoustic data, obtained in this study, could be used to argue for the interaction between magnesium and sulfate ions is given in Chapter VII. Following a similar procedure and using the results from the pressure measurements an extended study could also be made for understanding the pressure effect on ion-speciation in seawater.

## II. A TECHNIQUE TO MEASURE THE SOUND ABSORPTION OF THE PRIMARY RELAXATION PROCESS OF AQUEOUS MAGNESIUM SULFATE SOLUTIONS AT ELEVATED PRESSURES

### A. Introduction

Measurement of ultrasonic absorption is a powerful tool studying physical and chemical properties in solutions.<sup>2</sup> However, most of these measurements were made in high frequency regions ( $> 1$  MHz) and seldom were made under high pressures. Litovitz and Carnevale<sup>118</sup> have measured the sound absorption for water at pressures up to 2000 Kg/cm<sup>2</sup> using a pulse-echo technique in the MHz region. Fisher<sup>73,104,119</sup> made sound absorption measurements for .5M magnesium sulfate solution at pressures up to 1333 atm using the cylindrical resonator method in frequencies of 100 and 500 KHz.

Due to the desire to understanding the pressure effect on the sound absorption associated with the primary relaxation of the magnesium sulfate equilibrium and with the availability of a pressurizable titanium sphere, which meets pressure and frequency requirements, sound absorption measurements were made using the spherical-resonator method at frequencies from 30 to 300 KHz and at pressures of 1 to 307 atm for .02M magnesium sulfate solution,<sup>103</sup> magnesium sulfate and sodium chloride mixture<sup>99,103</sup> and artificial seawater.<sup>8</sup> For the background of the spherical-resonator method the reader is referred to Leonard,<sup>76</sup> Greenspan<sup>77</sup> and Stuehr.<sup>78</sup>

### B. Spherical Resonator

The resonator is a 105-liter titanium sphere manufactured in 1966 as a buoyancy vessel for the research submarine ALVIN. Its internal pressure limit is 307 atm. The internal surface of the sphere has been bead-blasted and acid-washed for better liquid adhesion and sound transmission. A sketch diagram of the sphere is shown in Fig. II.1, along with descriptions of its end caps and the ceramic transducers.

The two end caps have recessed wells to accommodate the thermistors that monitor the solution temperature at both ends of the sphere. O-ring grooves were made on each cap to provide pressure sealing. The top cap was also constructed to receive a high pressure fitting to allow for the pressurization of the fluid. The transducers were PZT ceramic products and were fastened by epoxy cement to the girth of the sphere, in equal distances with each member of the transducer pairs facing its counterpart on the diameters of the sphere. One pair of the transducers used 1.27 cm diameter 0.64 cm thick disks for 100-300 KHz operation, and the other pair used 1.27 cm diameter 0.953 cm thick disks for 30-100 KHz operation.

#### C. Pressure System

The block diagram of the pressure system is shown in Fig. II.2. All the equipment and accessories that contacted the solution and/or the hydraulic oil were made of No.316 stainless steel to avoid possible contamination of the solution. The combination of the dead-weight tester and the servo pump automatically monitors and compensates for the pressure decreases, along with a position sensor. The signal from the sensor will actuate the indicating needle to move away from its center line when a vertical displacement of the weight plate of the dead-weight tester was sensed. As soon as the needle indicates that the decrement of the pressure exceeds a pre-set value, the servo pump starts to move the piston of the pump to compensate for the reduced pressure until the pressure is back to normal. For the measurement at 307 atm, the observed pressure is maintained at  $307 \pm .000021$  atm, or more precisely,  $307 + .000021 \sin(.16t)$  atm, where  $t$  is in second.

#### D. Temperature Control

The arrangement for the temperature control is depicted in Fig. II.3. The following equipment is associated with maintaining a constant temperature: vacuum bell jar and base, water bath, transfer pump, stirring pumps, and refrigeration units. This equipment is enclosed in a thermal-isolated room where the room temperature is controlled by one refrigeration unit.

The bath is of the double boiler type with Glycol in the outer bath(300 liters) and water in the inner bath(500 liters). The stirring pumps constantly agitate the fluid in the two baths in order to maintain an uniform temperature. Heat is obtained from the heating elements controlled by the Thermotrols and a switch assembly. Another refrigeration unit is used to offset the heat in the outer bath. The inner bath is constructed with a flexible suction line that is connected to a 50 meter 2.54 cm-diameter coil pipe attached to the inner wall of the vacuum bell jar. The transfer pump forces the fluid from the inner bath through the coil pipe and returns it to the bath. After the bell jar is closed up the sphere is then surrounded by the coil pipe. Thus, the controlled bath temperature maintains the solution temperature. The temperature of the solution in the sphere is sensed by the thermistors mounted in the wells of the caps. The signals from the thermistors are then sent to a thermistor bridge and null detector unit, where the thermistor signals are further converted to a corresponding four digit display. The least significant digit indicates an increment of 1 is  $.015^{\circ}\text{C}$ . All controlling units for the system are located outside the thermal-isolated room. This enables the operator to make changes without interfering with the sphere environment. This arrangement of temperature control held temperature variation to  $.015\sin(.00175t)^{\circ}\text{C}$  at  $25^{\circ}\text{C}$ .

#### E. Reduction of Acoustic Losses

Major acoustic losses that can be reduced are those due to acoustic radiation and mechanical coupling. To avoid the radiation losses a vacuum was maintained at  $13.39 \times 10^{-4}$  atm inside the bell jar. Mechanical coupling losses were minimized by suspending the sphere with fine piano wire and also by reducing the size of the pressure tubing, the transducer units, and the signal transmission wires.

#### F. Electroacoustic System

The schematic diagram is shown in Fig. II.4. To produce the transmitting signal a digital synthesizer/function generator was used. It has the capability of digitally displaying the fre-

quency and the voltage of the sending signal and of setting and adjusting the frequency and the voltage by a simple key-in and/or push-button operation. The frequency resolution of this synthesizer is 1  $\mu$ Hz for operating frequencies below 100 KHz and 1 mHz elsewhere. Other than its high accuracy and stability features, this device provides the advantage of convenience in searching for the high-Q resonant modes because the operating frequency has to be varied continuously and also the receiver amplifier's oscillating frequency has to be kept in pace with the operating frequency. The quality of the sending signal was monitored through an oscilloscope at the output side of the power amplifier. The build-up of the resonant modes in the receiving channel was monitored by another oscilloscope. The oscilloscope (trigger-mode) was used to monitor the shape of decay of the received signal which would be recorded only when it was recognized to have both a good shape of decay and a reasonable decay rate.

#### G. Preparation of Solutions

Degassing of the solutions is necessary in order to make the solutions gas-free and to get rid of the bubbles that are possibly trapped at the interface of the solution and the container. The arrangement for the degassing of solution is depicted in Fig. II.5. For a solution of 100 liters it generally took 4 full days to complete the degassing job. For the salt solutions, once in awhile during the degassing processes water was replenished to compensate for the amount lost by evaporation so that the correct concentration of the solution was maintained. The completion of degassing was signaled by the occurrence of vapor cavitation bubbles. The loss of salt molecules due to water evaporation was negligible.

In the measurements, following the one for pure water, magnesium sulfate solutions as well as the subsequent mixtures of magnesium sulfate and sodium chloride were prepared without displacing the solution that was already in the sphere but rather by adding in directly the additional salt using the setup as shown in Fig. II.6. Mixing and degassing were also carried out with the same setup.

Another arrangement for preparing the solutions was to first complete the degassing of pure water in another vessel such as a glass sphere. The salt was then added in and was well dissolved by stirring. After the degassing was done the solution was then transferred to the titanium sphere where more degassing of the solution was done until it was completed. The solution was then ready for the pre-measurement routine.

#### H. Conditioning Temperature and Pressure

When the solution in the sphere was ready, the sphere was suspended and the desired pressure was applied. The bell jar was covered up and the vacuum was then applied inside the bell jar. The temperature control in the thermal-isolated room was kept constant at 25 °C. It generally took 3 days to allow the solution in the sphere to reach its temperature equilibrium at the operating temperature, confirmed by the achievement of a minimal temperature difference between the top and the bottom thermistor readings and the minimal variation of the operating temperature. The desired operating pressure was maintained by the automatic pressure control system. The pressure stability of  $\pm 0.000021$  atm was the key to success in maintaining temperature stability at elevated pressure.

#### I. Acquisition of Sound Absorption Data

The sound absorption data were obtained from the decay rate of the acoustic wave. The decay rates in water and in sodium chloride solutions were measured in order to secure the background losses which should be subtracted from the measured losses for magnesium sulfate solutions and from that for seawater as well. A quality factor of  $Q = 10^6$  has been observed in water measurements.<sup>79</sup> A sodium sulfate solution was measured in order to make certain how much it would contribute to the absorption measured in magnesium sulfate mixtures. However, a magnesium chloride solution was not measured because of its low concentration in the mixture, if any, and of its even more trivial absorption compared to sodium sulfate.<sup>3</sup> Since the water, the sodium chloride and the sodium sulfate solutions all showed negligible differences

among the decay rate results measured over the entire frequency region of our concern, and also because the differences between the sound speed in solutions and their corresponding background solutions are so trivial, the absorption data in terms of the absorption per wavelength was obtained from

$$\alpha\lambda = \frac{d_1 - d_2}{f} \quad (\text{II.1})$$

where  $\alpha$  in  $m^{-1}$  is the attenuation constant;  $\lambda$  in m, the wavelength of the sound wave in solution;  $d_1$  in  $sec^{-1}$ , the decay rate measured for the solution;  $d_2$  in  $sec^{-1}$ , the decay rate measured for the background solution; and  $f$  in Hz is the operating frequency of the acoustic wave.

A theoretical curve of the absorption<sup>1,2</sup> may be expressed by

$$\alpha\lambda = \frac{2(\alpha\lambda)_m f f_r}{f^2 + f_r^2} \quad (\text{II.2})$$

where  $(\alpha\lambda)_m$  is the  $\alpha\lambda$  when  $f = f_r$ , the relaxation frequency. The maximum absorption,  $(\alpha\lambda)_m$ , and the relaxation frequency,  $f_r$ , was obtained by a curve fitting process using the measured data of  $\alpha\lambda - f$  pairs.

#### J. Accuracy of Measurements

Among the results from the pressure measurements of the three different solutions, the seawater result showed the largest decrease on  $(\alpha\lambda)_m$ , 26.3 %, for the pressure increase from 1 to 307 atm. According to this information, the effect of pressure on  $(\alpha\lambda)_m$  is estimated to be  $9 \times 10^{-4}$  % per 1 % change in pressure (atm). Thus, at 307 atm the error due to the pressure ripples is estimated to be  $\pm 6 \times 10^{-9}$  %, based on the pressure variation cited earlier.

According to the results of the sound absorption measurements by Wilson,<sup>115</sup> the temperature effect on  $(\alpha\lambda)_m$  is .86 % per 1 % change in temperature ( $^{\circ}C$ ). Therefore, for the variation on temperature as cited earlier the error on  $(\alpha\lambda)_m$  due to temperature variation is  $\pm .05$  %.



The error on  $(\alpha\lambda)_m$  associated with the concentration error is estimated to be .4 % per 1 % change in concentration (M) because the sound absorption is approximately proportional to the concentration of magnesium sulfate in the solution. Thus, for a decrease of .12 % in concentration due to the expansion of solution for a temperature increase of 5 °C, there would be a decrease of .05 % on  $(\alpha\lambda)_m$ .

The error on  $(\alpha\lambda)_m$  due to neglecting the sound speed differences for the background solution is estimated to be an increase of .08 %.

Assuming that a  $\pm 1$ . % error on the measured decay rate is caused by the electroacoustic system, the induced error on  $(\alpha\lambda)_m$ , correspondingly, is estimated to be  $\pm 2$ . %.

The accuracy of the maximum absorption was obtained from the least-square-root curve fitting program used for securing the value of the maximum absorption (see Eq. (II.2)). A similarly logical procedure, however, is not possible for the determination of the relaxation frequency. Therefore, the accuracy of relaxation frequency was analyzed with a different process. The maximum absorption obtained was the one with a minimum standard deviation from the curve fitting program. By shifting the relaxation frequency away from the frequency where this maximum absorption is located the curve fitting program would give a new value for the maximum absorption with a larger standard deviation. Dividing this new value,  $\sigma$ , by the initial minimum standard deviation,  $\sigma_o$ , a number greater than 1 would be obtained. This number would represent a statistical index reflecting the degree of certainty of the curve fitting result. After examination of the results from all of the measured solutions,  $\sigma/\sigma_o = 1.21$  was found to be the limit value where a maximum error of the relaxation frequency is addressed. The curve-fitting results reflect an error on  $(\alpha\lambda)_m$  on the average of  $\pm 1.1 \pm .3$  %. The maximum error of the relaxation frequency obtained through the curve-fitting process is estimated to be on the average of  $\pm 9.6 \pm 4.1$  %.

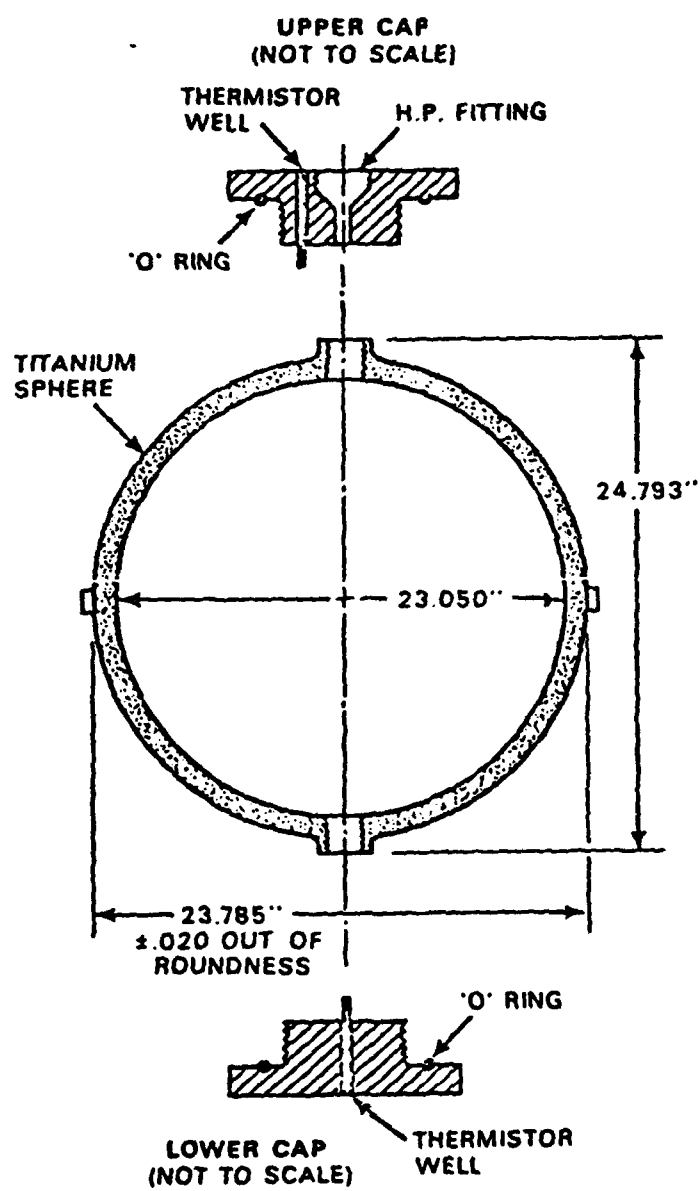


Figure II.1 Sketch diagram of the titanium sphere and its peripheral accessories.

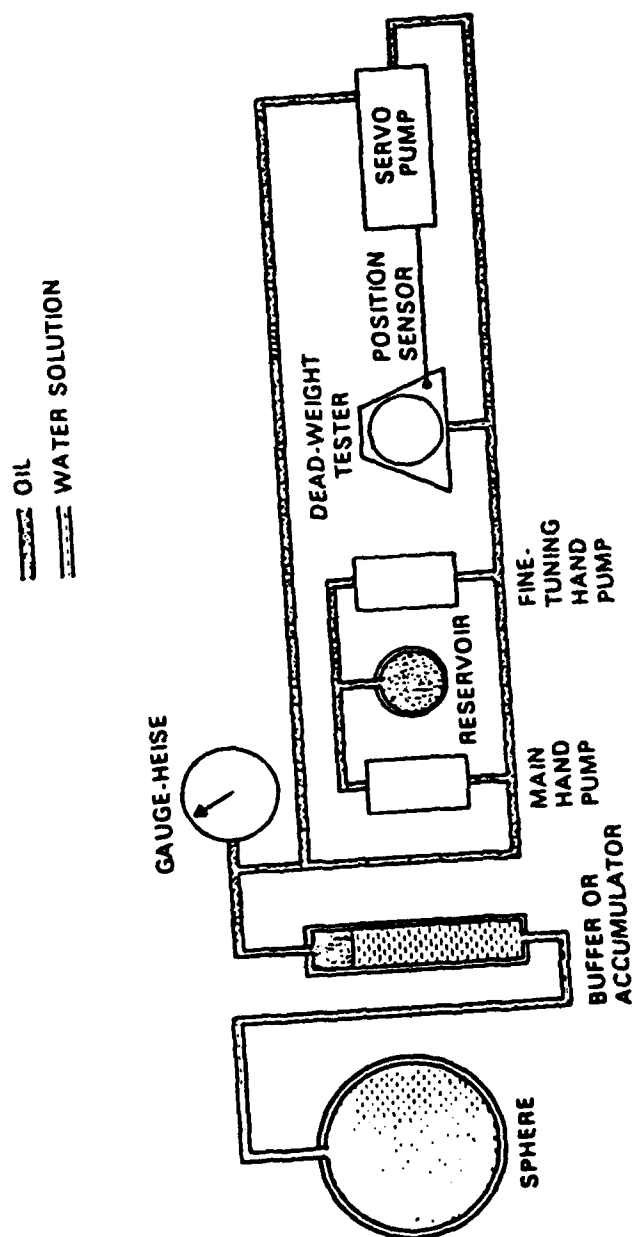


Figure 11.2 Block diagram of the pressure system.

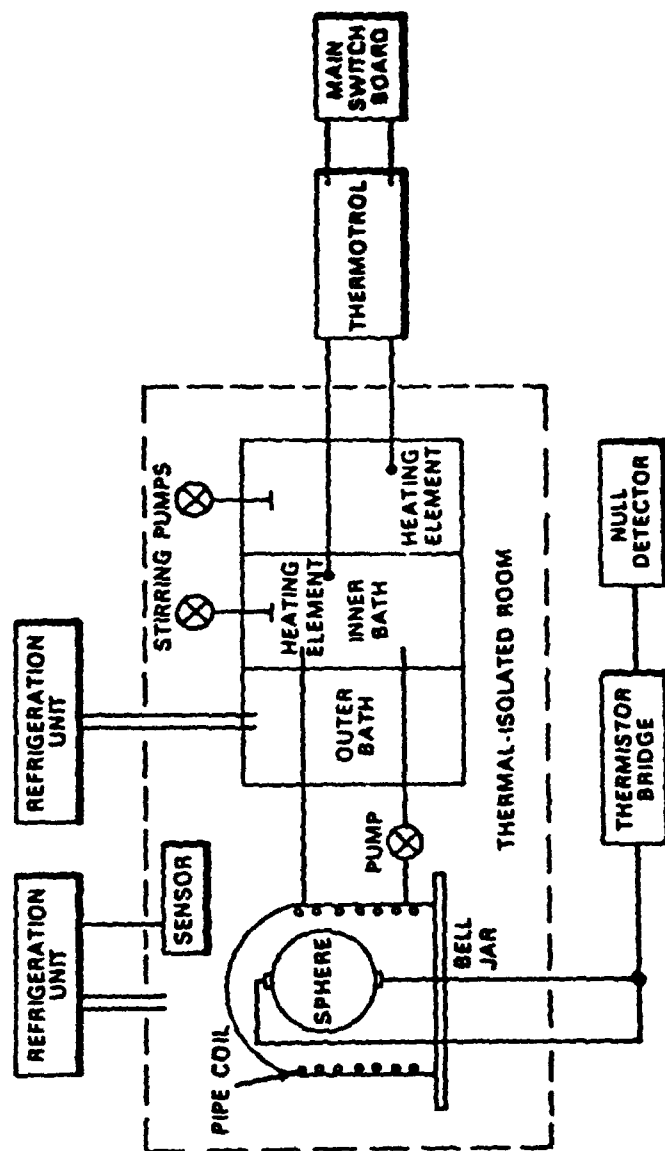


Figure 11.3 Block diagram of the temperature control system.

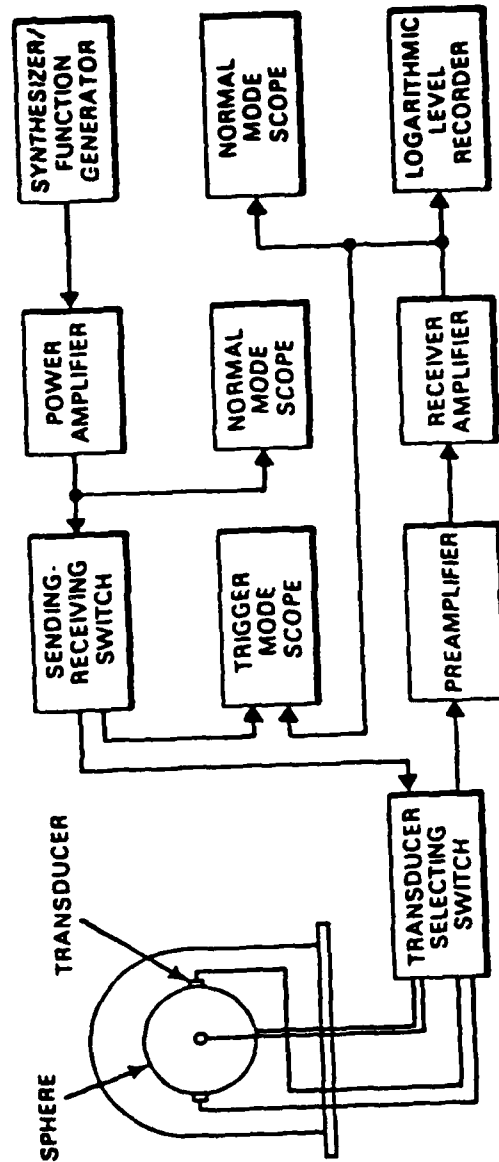


Figure 11.4 Block diagram of the electroacoustic system.

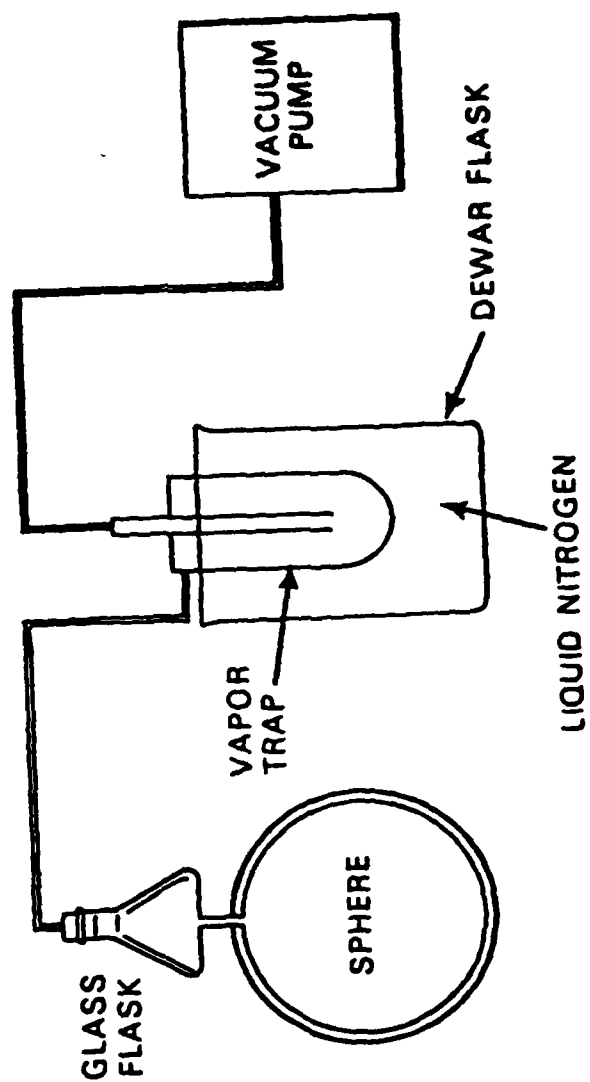


Figure 11.5 Block diagram of the degassing apparatus.

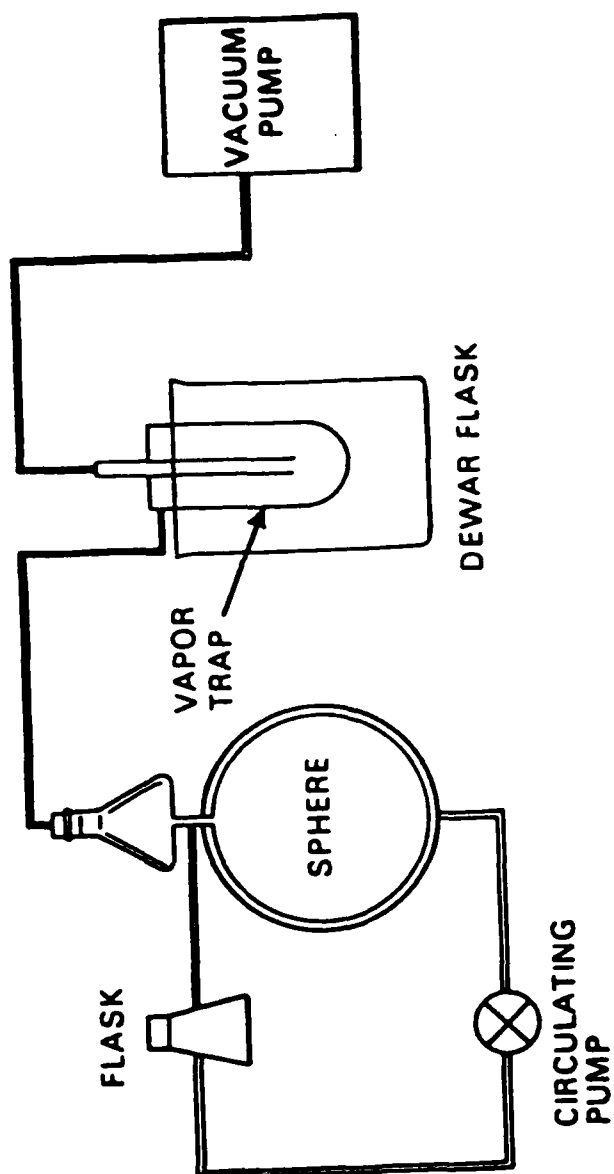


Figure 11.6 Block diagram of the degassing and mixing apparatus.

### III. SOUND ABSORPTION IN SODIUM CHLORIDE AND SODIUM SULFATE SOLUTIONS

#### A. Introduction

The many studies of electrolyte solutions found that the thermodynamic dissociation constants at 25 °C are: .00399 to .0070 for magnesium sulfate,<sup>17-30</sup> .1 to .596 for sodium sulfate,<sup>14-16,30-35</sup> .178 to 9.55 for magnesium chloride<sup>14-16,36</sup> and .943 to 40 for sodium chloride.<sup>37-45</sup> Evidence of  $MgSO_4^0$  and  $NaSO_4^-$  ion-pairs<sup>69,70,120</sup> have been obtained by Raman spectroscopy studies. This situation leads to a consideration of the equilibria associated with  $MgSO_4^0$ ,  $NaSO_4^-$ ,  $MgCl^0$  and  $NaCl^0$  ion-pairs where sound absorption in magnesium sulfate-sodium chloride solutions or seawater is concerned.

The early sound absorption measurements of electrolyte solutions were made in the frequency region of several MHz.<sup>6,7</sup> The results, which were expressed in  $\alpha/f^2$ , showed that, in general, the sound absorption of magnesium sulfate solution exceeds the water value by a factor of 4; a factor of 2 for sodium sulfate and of magnesium chloride, it only slightly exceeds the water value. That of sodium chloride, however, is slightly less than the water value. These results counted as a whole the sum of the classical and the excess absorptions for solutions of a moderate concentration. In the region of 100 KHz the .5M magnesium sulfate solution was found to show a maximum excess absorption that exceeded the water value by a factor of 80. No presence of the excess absorption in sodium sulfate, magnesium chloride and sodium chloride solutions were reported.<sup>3,76,80</sup> Magnesium sulfate solutions were found to show a second excess absorption maximum in the 200 MHz region.<sup>3</sup> In this region sodium sulfate solutions of higher concentrations were also found to show an absorption maximum.<sup>9</sup> However, for those of concentrations less than .1M, sound absorption was not detected.

The excess sound absorption is originated from the pressure-dependent relaxation process associated with the chemical equilibrium in solutions.<sup>1,2,10</sup> The generalized form of the excess absorption per wavelength is expressed by



$$\alpha\lambda = \sum_i \frac{2(\alpha\lambda)_{m,i} f f_{r,i}}{f^2 + f_{r,i}^2} \quad (\text{III.1})$$

where  $(\alpha\lambda)_{m,i}$  is the maximum absorption per wavelength of the  $i$ -th relaxation process, of which the relaxation frequency is  $f_{r,i}$ . Then, according to the observations mentioned above, the excess absorption per wavelength for magnesium sulfate solutions is

$$\alpha\lambda = \frac{2(\alpha\lambda)_{m,1} f f_{r,1}}{f^2 + f_{r,1}^2} + \frac{2(\alpha\lambda)_{m,2} f f_{r,2}}{f^2 + f_{r,2}^2} \quad (\text{III.2})$$

and that of sodium sulfate solutions is

$$\alpha\lambda = \frac{2(\alpha\lambda)_m f f_r}{f^2 + f_r^2} \quad (\text{III.3})$$

For magnesium chloride or sodium chloride solutions,  $\alpha\lambda$  is small because either the  $f_r$  is too small or too large in the frequency region mentioned or the  $(\alpha\lambda)_m$  is too small a value due to the characteristics of these two solutions.

## B. Results

During the investigation of sound absorption in magnesium sulfate-sodium chloride solutions of  $[MgSO_4] = .02M$  and  $[NaCl] = 0$  to  $.12M$  in the region of 100 KHz, sound absorption measurements were also made for  $.16M$  sodium chloride and  $.03M$  sodium sulfate solutions.<sup>8</sup> The results obtained by using the spherical resonator method are shown in Fig. III.1. The corresponding plot of  $\alpha/f^2$  is given in Fig. III.2. The raw data of measured decay rates and calculated  $\alpha/f^2$  values of this work are given in Appendix C. It can be seen from Figures III.1 and III.2 that the excess absorption of these two solutions is not distinguishable from that of water. Hence, the sound absorption due to the equilibria associated with  $NaSO_4^-$  and  $NaCl^0$  ion-pairs in the above-mentioned magnesium sulfate-sodium chloride solutions is negligible.

The sound absorption under pressure was also measured for  $.58M$  sodium chloride solution at pressures from 1 to 307 atm.<sup>8</sup> The results are shown in Fig. III.3. The correspond-

ing  $\alpha/f^2$  plot is given in Fig. III.4. It shows that the sound absorptions in .58M sodium chloride solution at pressures up to 307 atm are comparable to that of water, the difference of the sound absorptions between the .58M sodium chloride solution and water is not detected by the sound absorption measurement. These results are useful when corrections for the measured absorption are to be made and the sound absorption due to the sodium chloride equilibrium in solutions is questioned.

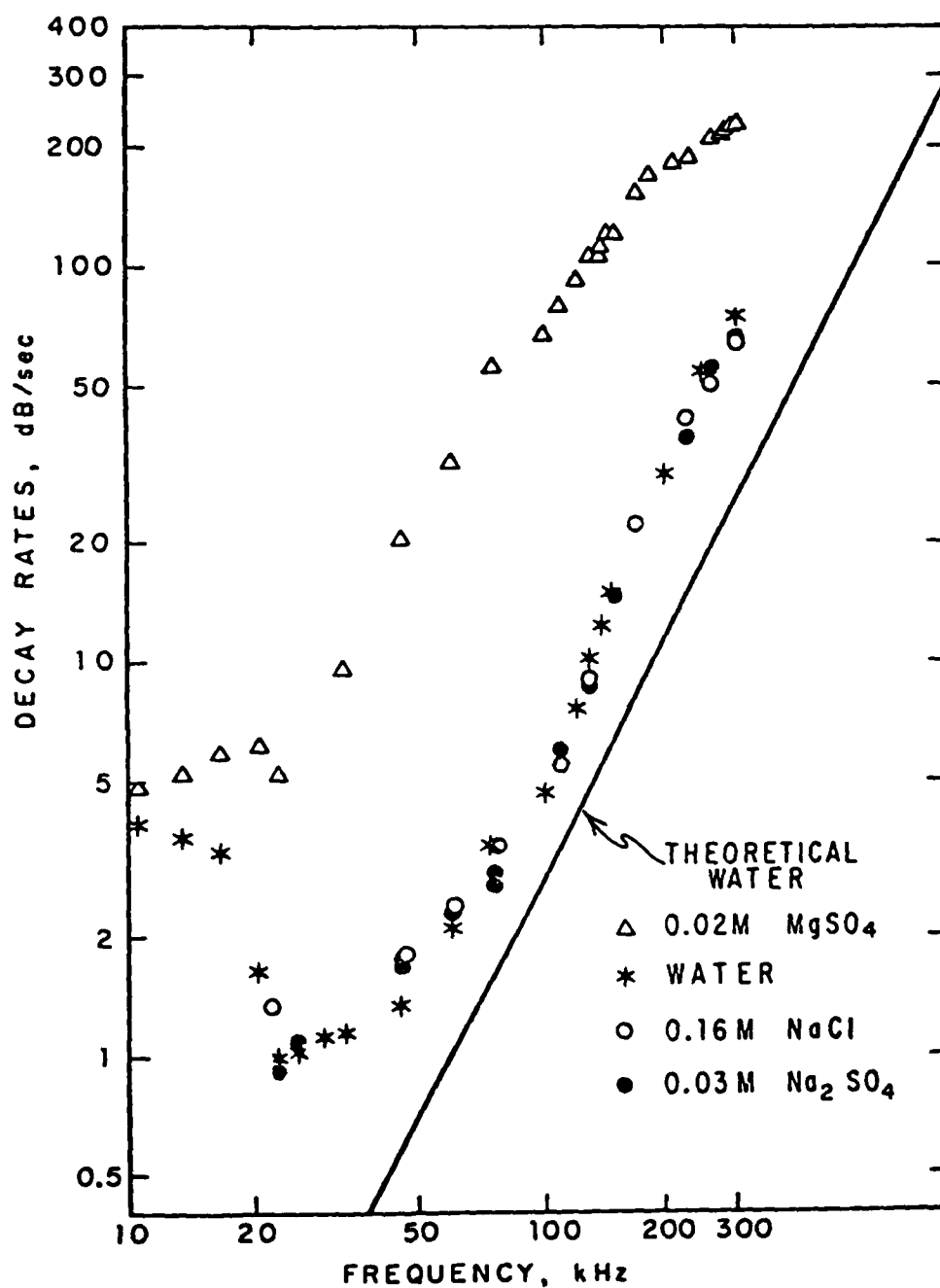


Figure III.1 Measured decay rates of sound waves in water, .16M sodium chloride, .03M sodium sulfate and .02M magnesium sulfate solutions.

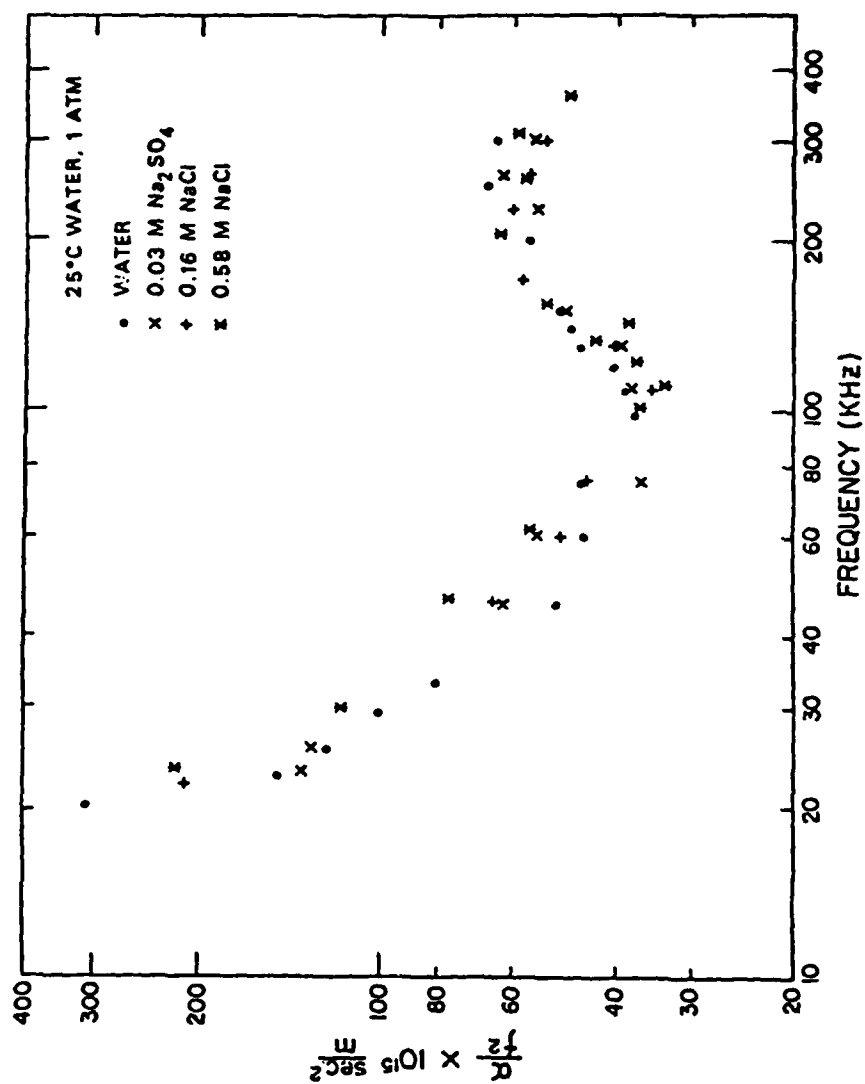


Figure III.2 Absorption per frequency square calculated for water, .03M sodium sulfate, .16M sodium chloride and .58M sodium chloride solutions.

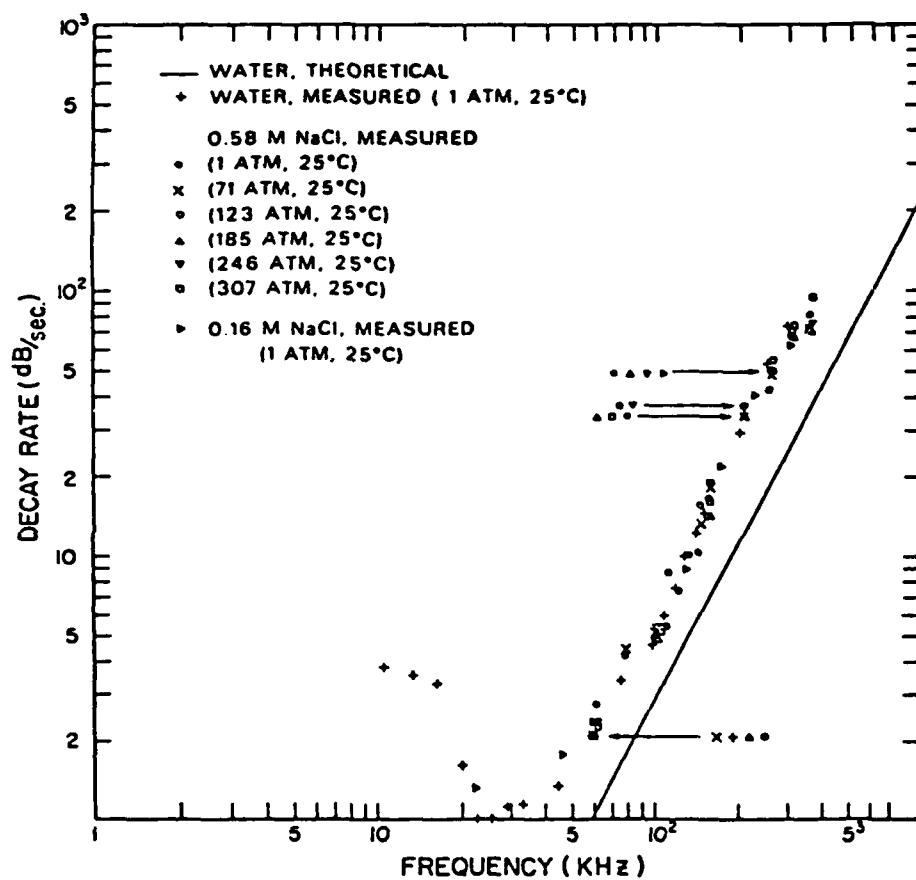


Figure III.3 Measured decay rates of sound waves in water and .16M sodium chloride solution at 1 atm, and .58M sodium chloride solution at 1, 71, 123, 185, 246 and 307 atm.

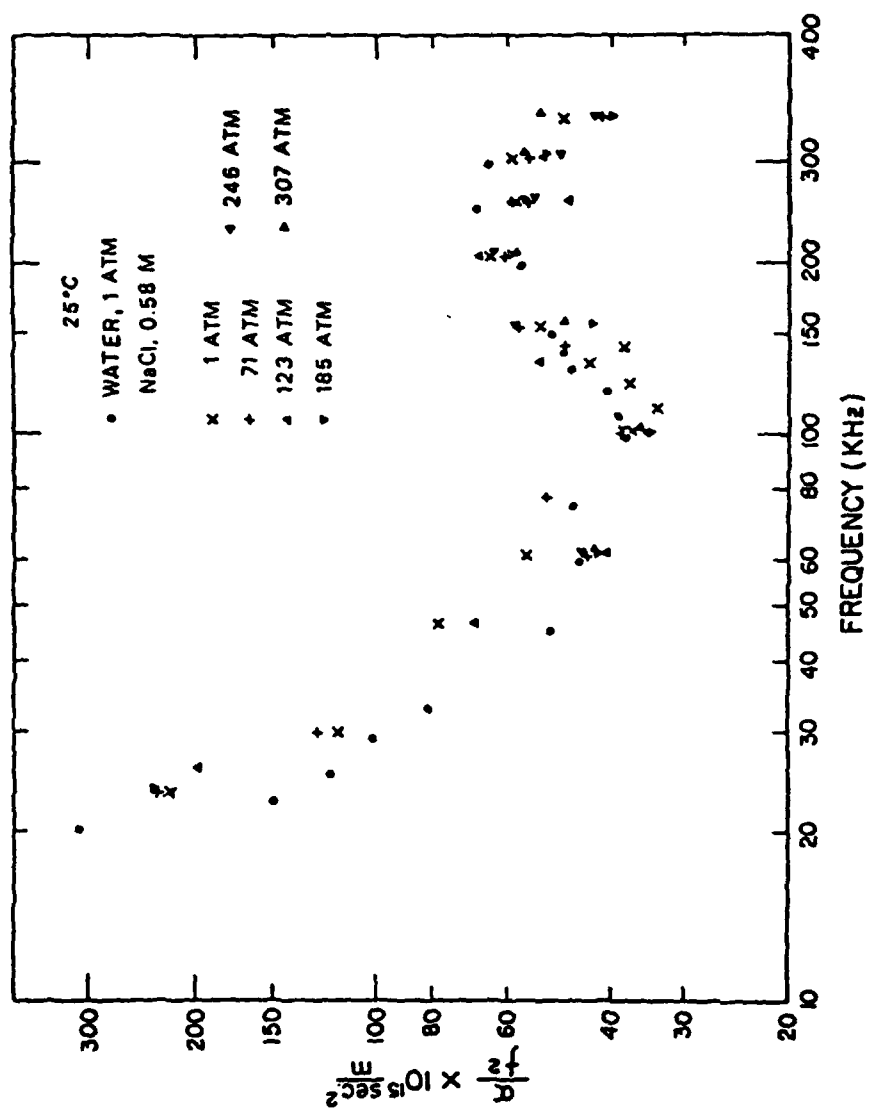


Figure III.4 Absorption per frequency square calculated for water at 1 atm and .58M sodium chloride at 1, 71, 123, 185, 246 and 307 atm.

#### IV. DIFFERENTIAL SOUND ABSORPTION TECHNIQUE FOR ION-PAIRING STUDIES IN AQUEOUS SOLUTIONS OF MAGNESIUM SULFATE AND SODIUM CHLORIDE AT 25 °C and 1 atm

##### A. Introduction

Aqueous magnesium sulfate solutions exhibit a sound absorption maximum in the neighborhood of 150 KHz which is due to the pressure-dependent chemical relaxation process associated with the equilibrium between  $Mg^{++}$  and  $SO_4^{--}$  ions and  $MgSO_4^{\pm}$  ion-pairs.<sup>1,2</sup> Kurtze and Tamm<sup>3</sup> found that this sound absorption maximum in magnesium sulfate solution, however, is reduced by the addition of sodium chloride and, hence, differential sound absorption is produced. The addition of sodium chloride not only increases the ionic strength of the solution but also results in two additional equilibria relevant to  $NaSO_4^-$  and  $MgCl^+$  ion-pairs; both of these two effects tend to reduce the  $MgSO_4^{\pm}$  ion-pairs and, hence, the sound absorption in solutions.<sup>3-5</sup> When the concentrations of the salts are not high, the sodium chloride itself does not contribute to the sound absorption. Sound absorption due to the  $NaSO_4^-$  and  $MgCl^+$  ion-pairs is negligible compared to that due to  $MgSO_4^{\pm}$ . No excess sound absorption in sodium chloride solutions has been reported.<sup>2,3,6-8</sup> The primary absorption maximum of a .5M magnesium sulfate solution<sup>3</sup> exceeds the water value by a factor of 80, and in the same frequency region, sound absorption in sodium sulfate solutions of concentrations less than .1M is comparable to the water value.<sup>3,8,9</sup> The magnesium chloride solutions exhibit less sound absorption than sodium sulfate solutions do when the two different solutions are of equal concentration.<sup>3,5,6</sup> Thus, the sound absorption of solutions measured in this work can be attributed solely to the magnesium sulfate equilibrium. Since there are finite relationships between the sound absorption and the  $MgSO_4^{\pm}$  ion-pair concentration, which can be determined by the sound absorption theory,<sup>10</sup> and also between the concentrations of  $MgSO_4^{\pm}$  ion-pairs and other ion-pairs in the solution, which can be determined by electrolyte theory,<sup>11-13</sup> the sound absorption data may then be used as a measure of the ion-pair concentrations in magnesium sulfate-sodium chloride

solutions. Examinations of sound absorption theory<sup>10</sup> found that the sound absorption associated with the magnesium sulfate equilibrium may be assumed to be in proportion to  $MgSO_4^0$  ion-pair concentration in the solution.

This study is concerned with the role of the unsymmetrical ion-pairs,  $NaSO_4^-$  and  $MgCl^+$ , in  $MgSO_4-NaCl$  system as well as with other similar unsymmetrical ion-pairs in other systems that resemble the  $MgSO_4-NaCl$  system;<sup>14-16</sup> for example, the  $KSO_4^-$  in  $MgSO_4-KCl$  system. This study thus provides a means based on acoustic data for checking the ion-pairing of these unsymmetrical ion-pairs.

The reported dissociation constants and the activity coefficients for  $MgSO_4^0$ ,  $NaSO_4^-$ ,  $MgCl^+$  and  $NaCl^0$  ion-pairs are diverse<sup>14-47</sup> as are the approaches for estimating the activity coefficients of the ions<sup>48-59</sup> in solutions, especially in a mixture. Recognizing these existing difficulties, this study intends to confine the approach used for estimating the  $MgSO_4^0$  ion-pair concentration to a self-consistent ion-association model that is based on the framework of and the results from the conductance works on  $MgSO_4$ ,  $Na_2SO_4$ , and  $MgCl_2$  dissociations by Fisher<sup>14</sup> and Fisher and Fox.<sup>15-17</sup> In these works Kurtze and Tamm's<sup>3</sup> absorption data on the  $MgSO_4-NaCl$  system were used in order to decide on a reasonable distance parameter in fitting the conductance data to the theory. Thus, this study is expected to test the results obtained from these conductance studies and to develop a model that is self-consistent and is supported by both the conductance data and the differential sound absorption data.

Kurtze and Tamm<sup>3</sup> expressed their differential sound absorption results with an empirical equation of

$$\frac{\Delta\alpha}{\alpha} = \frac{\alpha_0 - \alpha}{\alpha} = \frac{[NaCl]}{[MgSO_4]} f \quad (IV.1)$$

where  $\alpha_0$  is the sound absorption constant in the pure solution,  $\alpha$  is that in the mixture,  $[ ]$  denotes the formal concentration of the salt and  $f$  is a factor of constant. Their measurements were made at 20 °C. The data obtained consists of 2 data points in  $[MgSO_4] = .017M$ , 11 data



points in  $[MgSO_4] = .1M$  and 3 data points in  $[MgSO_4] = .17M$ , in the region of  $[NaCl]/[MgSO_4] = 2$  to 30. According to these data a constant of  $f = .21$  was claimed by Kurtze and Tamm.

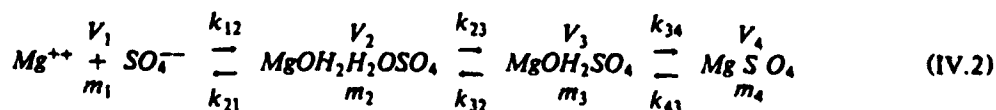
The initial theoretical analysis made by Neuberger, Hsu and Fisher<sup>5</sup> found that the  $F$ -number for the differential  $MgSO_4$  ion-pair concentration, which plays the same function as the  $f$ -number for the differential sound absorption in Eq. (IV.1), is not a single constant number but a constant which varies with the formal concentration of magnesium sulfate. This result, as reflected in the differential sound absorption, is then in conflict with Kurtze and Tamm's observation.

Also, in seawater, sound absorption is closely tied to the interactions between magnesium sulfate and sodium chloride as well as to other salts in seawater.<sup>59-61</sup> The  $MgSO_4-NaCl$  system contains the major constituents of seawater and acts as the background base of sound absorption in seawater. Studies of this system are essential to understanding sound absorption in seawater.<sup>59-61</sup> The present study represents an initial effort in this area.

#### B. Sound Absorption and Ion-pairs

The sound absorption theory based on a 4-state association model<sup>10</sup> shows that the maximum absorption per wavelength due to the magnesium sulfate equilibrium is related to a function of the concentrations of the various species involved in the equilibrium. Both the sound absorption theory<sup>2,62-67</sup> and the 4-state association model<sup>68-75</sup> which the sound absorption theory is based on have been widely used in the fields of relaxation kinetics in electrolyte solutions.

The 4-state association model which Eigen and Tamm<sup>10</sup> proposed for interpreting the absorption data from Kurtze and Tamm<sup>3</sup> for magnesium sulfate solutions is



where  $V_i$  and  $m_i$  are the partial volumes and the concentrations of the species in states 1,2,3 and 4, respectively, and  $K_{ij}$  are the reaction rates.

According to Eigen and Tamm, the primary relaxation process in magnesium sulfate solutions is due to the equilibrium between states 3 and 4, and the sound absorption per wavelength is expressed by

$$\alpha\lambda = \frac{\pi}{\beta_0} \frac{(m'_1 + m_2 + m_3)m_4}{(m'_1 + m_2 + m_3 + m_4)} \frac{(\Delta V_{III})^2}{RT} \frac{\omega\kappa}{\omega^2 + \kappa^2} \quad (\text{IV.3})$$

where  $\alpha$  is the absorption constant,  $\lambda$  is the wavelength of the sound wave,  $\beta_0$  is the static compressibility of the solution,  $\Delta V_{III}$  is a function of the volume changes and the reaction rates of the equilibria,  $m'_1 = m_1[2 + (\partial \ln \pi^f / \partial \ln m_1)]^{-1}$  is the concentration of the species in state 1 when activity coefficients are considered,  $\pi^f = f_{Mg^{++}} f_{SO_4^{--}} / f_{MgSO_4}$ ,  $f_i$  is the activity coefficients of the ion and the ion-pair,  $R$  is the gas constant,  $T$  is the temperature,  $\omega = 2\pi f$ ,  $f$  is the frequency of the sound wave,  $\kappa = 2\pi f_r$ , and  $f_r$  is the relaxation frequency.

When  $\omega = \kappa$ ,  $\alpha\lambda$  has a maximum value of  $(\alpha\lambda)_m$ , which is the maximum sound absorption per wavelength, then Eq. (IV.3) can be written as

$$\alpha\lambda = \frac{2(\alpha\lambda)_m f f_r}{f^2 + f_r^2} \quad (\text{IV.4})$$

The concentration of unhydrated  $MgSO_4$  ion-pairs is small as compared with the total concentration of all the magnesium sulfate species of the equilibrium.<sup>68,71-75</sup> In .02M magnesium sulfate solution, calculations show that less than 1% of the total magnesium sulfate species concentration is unhydrated ion-pairs. Thus,  $m'_1 + m_2 + m_3 + m_4 \approx m'_1 + m_2 + m_3$  and the maximum sound absorption per wavelength associated with the primary absorption relaxation of the  $MgSO_4$  equilibrium may then be approximated by

$$(\alpha\lambda)_m = \frac{\pi}{2\beta_0} m_4 \frac{(\Delta V_{III})^2}{RT} \quad (\text{IV.5})$$

Since  $m_4$  is approximately proportional to the total  $MgSO_4$  ion-pair concentration,

$[MgSO_4^*]$ , the sound absorption then becomes proportional to the total  $MgSO_4^*$  ion-pair concentration if the physical properties of solutions considered are comparable. Consequently, the differential sound absorption can be related to the differential ion-pair concentration by the following equation:

$$\frac{\Delta(\alpha\lambda)_m}{(\alpha\lambda)_m} = \frac{\Delta[MgSO_4^*]}{[MgSO_4^*]} \quad (IV.6)$$

where  $\Delta(\alpha\lambda)_m = (\alpha\lambda)_{m,o} - (\alpha\lambda)_m$ ,  $\Delta[MgSO_4^*] = [MgSO_4^*]_o - [MgSO_4^*]$ ,  $(\alpha\lambda)_{m,o}$  and  $[MgSO_4^*]_o$  are the maximum absorption per wavelength and the total  $MgSO_4^*$  ion-pair concentration of the original magnesium sulfate solution, and  $(\alpha\lambda)_m$  and  $[MgSO_4^*]$  are that of the solution after the addition of sodium chloride.

The total  $MgSO_4^*$  ion-pair concentration can be obtained by using an ion-association model that is incorporated with the recently reported dissociation constants from conductance data and the same Debye-Hückel equations for the activity coefficients in analyzing the conductance data in measurements involving  $MgSO_4^*$ ,  $NaSO_4^-$  and  $MgCl^+$  ion-pairs.<sup>15-17</sup>

The empirical equation which Kurtze and Tamm used in relating the differential sound absorption data and the concentration ratio,  $[NaCl]/[MgSO_4]$ , is also used in this study for a simple expression of the results. For convenience, the absorption constant,  $\alpha$ , is replaced by the maximum sound absorption per wavelength,  $(\alpha\lambda)_m$ , and this empirical equation then becomes

$$\frac{\Delta(\alpha\lambda)_m}{(\alpha\lambda)_m} = F \frac{[NaCl]}{[MgSO_4]} \quad (IV.7)$$

This equation enables one to represent the differential sound absorption by using a simple  $F$ -number as the  $f$ -number does in the Kurtze and Tamm<sup>3</sup> paper. A similar equation which enables one to represent the differential ion-pair concentration is

$$\frac{\Delta[MgSO_4^*]}{[MgSO_4^*]} = F \frac{[NaCl]}{[MgSO_4]} \quad (IV.8)$$

### C. Sound Absorption Measurements

Measurements were carried out at 25 °C and 1 atm using the spherical resonator method. A sphere is used as a solution container in which the sound wave in solution is excited in the resonant mode. Sound absorption is measured in terms of the decay rates of the pressure magnitude of sound waves. After the excitation wave is cut off, the decay rate of the received signal is recorded. The absorption of a solution meeting the background correction base is also measured. The residue of sound absorption obtained by subtracting the sound absorption of the background solution from that of the test solution would be the excess sound absorption sought. For the background of the spherical resonator method the reader is referred to Leonard,<sup>76</sup> Kurtze and Tamm,<sup>3</sup> Greenspan,<sup>77</sup> and Stuehr.<sup>78</sup>

The measuring apparatus is depicted in Fig. IV.1, where the resonator is a 105-liter titanium sphere. The major features of this apparatus setup are:

a. An improved temperature-maintaining capacity: The water bath is of the double boiler type with Glycol in the outer bath and water in the inner bath. The inner bath is constructed with a flexible suction line that is connected to the coil pipe attached to the inner wall of the vacuum bell jar. The transfer pump forces the fluid from the inner bath through the coil pipe and returns to the bath. After the bell jar is closed, the sphere is then surrounded by the coil pipe. Thus, the controlled bath temperature reflects onto the sphere and the solution temperature is better maintained. With this arrangement the temperature of the solutions was held to within a deviation of  $\pm .03$  °C.

b. An accurate temperature reading of the solution: The two end caps at the top and the bottom of the sphere have recessed wells to accommodate the thermistors that sense the temperature of the solution at both ends of the sphere. The thermistor monitor converts the signal from the thermistor to a digital display showing the temperature sensed by the thermistor. The solution temperature was assumed to be the mean of the readings from the two thermistors.

c. A digitally displayed signal generator/synthesizer: The synthesizer has the capability of digitally displaying the frequency and voltage of the sending signal and of setting and adjusting the frequency and voltage by simply a key-in and/or push-button operation. The frequency resolution of this synthesizer is 1  $\mu$ Hz for operating frequencies below 100 KHz and is 1 mHz elsewhere. Besides its high accuracy and stability, this device provides the advantage of convenience in searching for the high-Q resonant modes. A quality factor of  $Q = 10^6$  has been obtained at 25 KHz in water measurements.<sup>79</sup>

The decay rates of sound waves in the frequency region of 10 to 300 KHz were measured for the following solutions: a. Deionized water. b. .16 M NaCl. c. .03M  $Na_2SO_4$ . d. .02M  $MgSO_4$ . e. .02M  $MgSO_4$  + .02M NaCl. f. .02M  $MgSO_4$  + .04M NaCl. g. .02M  $MgSO_4$  + .08M NaCl. h. .02M  $MgSO_4$  + .12M NaCl. All of the solutions were prepared from AR-rated reagents and deionized water and were degassed. The decay rates obtained from water and sodium chloride solution were combined to set a background correction base. The actual decay rates of the magnesium sulfate solutions were converted to sound absorption data expressed in absorption per wavelength,  $\alpha\lambda$ . The maximum absorption per wavelength,  $(\alpha\lambda)_m$ , and the relaxation frequency,  $f_r$ , were obtained from the least-square-root fitting program for the  $\alpha\lambda$  data to the theoretical equation of Eq. (IV.4). The  $(\alpha\lambda)_m$  data were then used to calculate the  $\Delta(\alpha\lambda)_m/(\alpha\lambda)_m$  and the  $F$ -numbers, according to Eq. (IV.7).

The error of the measured  $(\alpha\lambda)_m$  is estimated to be 5-10 %. The error of the  $\Delta(\alpha\lambda)_m$  is presumably smaller than that of  $(\alpha\lambda)_m$  due to the cancellation of the system error.

#### D. Theoretical Estimation

The equilibria in the solutions under consideration are



and



The thermodynamic dissociation constant,  $K_{MN}$ , is expressed by

$$K_{MN} = \frac{[M][N]f_{\pm MN}^2}{[MN]f_{MN}} \quad (\text{IV.12})$$

where  $f_{\pm MN}$  is the mean activity coefficient of ions  $M$  and  $N$ , and  $f_{MN}$  is the activity coefficient of ion-pairs.

The mean activity coefficient is obtained from

$$-\log f_{\pm MN} = \frac{A |Z_M Z_N| I^h}{1 + Bd I^h} \quad (\text{IV.13})$$

where  $Z_{i,i=M,N}$  is the valence of the ions  $A$  and  $B$  are the usual Debye-Hückel constants,  $d$  is the distance parameter and  $I$  is the ionic strength expressed by

$$I = \frac{1}{2} \sum_i Z_i^2 [C_i] \quad (\text{IV.14})$$

where  $C_i$  includes all of the charged species in solution.

The activity coefficient of the  $\text{MgSO}_4^0$  ion-pairs is assumed to be unity and that of singly-charged ion-pairs are obtained from

$$-\log f_{MN} = \frac{A I^h}{1 + Bd I^h} \quad (\text{IV.15})$$

The dissociation constants and the distance parameters obtained from the conductance works and used in this ion-association model are:<sup>15-17</sup>  $K_{MN} = .0062$ ,  $.1$  and  $.178$  for  $\text{MgSO}_4^0$ ,  $\text{NaSO}_4^-$  and  $\text{MgCl}^+$ , respectively, and  $d = 11.58\text{\AA}$ ,  $7.14\text{\AA}$  and  $3.57\text{\AA}$  for 2-2 pairing, 1-2/2-1 pairing and singly-charged ion-pairs, respectively.

The concentration of the  $\text{MgSO}_4^0$  ion-pairs is obtained by iterative approximation using Eqs. (IV.9) to (IV.15). The differential  $\text{MgSO}_4^0$  ion-pair concentration and the corresponding  $F$ -number are then calculated according to Eq. (IV.8).

## E. Results and Discussions

The measured decay rates of sound waves in water, .02M magnesium sulfate, .16M sodium chloride, and .03M sodium sulfate solutions are plotted in Fig. IV.2. The raw data of the decay rates measured for these solutions are given in Appendixes B and C. It shows that the decay rates in .16M sodium chloride and .03M sodium sulfate solutions are comparable to that in water. This observation is in agreement with other results.<sup>3,6-9</sup> It thus confirms that the sound absorption in  $MgSO_4$ - $NaCl$  solutions, measured in this research, can be attributed only to the magnesium sulfate equilibrium in the solutions, since these solutions would contain less sodium chloride than a .16M sodium chloride solution does and also less sodium sulfate than a .03M sodium sulfate solution does.

The sound absorption data obtained for the  $MgSO_4$ - $NaCl$  solutions and their theoretically-fitted curves are plotted in Fig. IV.3 to Fig. IV.7. The sound absorption data and the curve fitting results are shown in Appendix D. The results of the pure magnesium sulfate solution is in agreement with that by Wilson and Leonard.<sup>80</sup> The corresponding maximum absorption,  $(\alpha\lambda)_m$ , the  $F$ -number and the  $\Delta(\alpha\lambda)_m/(\alpha\lambda)_m$  of the measured solutions as well as the  $MgSO_4$  ion-pair concentration, the  $F$ -number and the  $\Delta[MgSO_4]/[MgSO_4]$ , predicted from the theory, are summarized in Table IV.1. Further plotted in Fig. IV.8 are the data of the maximum absorption and the  $MgSO_4$  ion-pair concentration, and in Fig. IV.9 are the differential absorption and the differential  $MgSO_4$  ion-pair concentration. These two figures demonstrate the agreement of the results from the measurement with those of the theoretical estimation. Kurtze and Tamm's measured results of  $\Delta\alpha/\alpha$  are plotted in Fig. IV.9 also.

Due to the use of the simple Debye-Hückel equation in the theoretical estimation of the ion-pair concentration, the results must be handled cautiously. Although the calculation of the differential  $MgSO_4$  ion-pair concentration has been carried up to  $[NaCl]/[MgSO_4]=30$ , only the results of  $[NaCl]/[MgSO_4]<6$  for  $[MgSO_4]=.02M$  and of  $[NaCl]/[MgSO_4]<3$  for  $[MgSO_4]=.1M$  are considered to be within an acceptable tolerance. Beyond these concentration ranges the results are in need of further justification.

According to the ion-association model and assuming different degrees of dissociation of the two unsymmetrical ion-pairs in the solution, estimation of the  $F$ -number has been made for the case of  $[NaCl]/[MgSO_4] = 1$ . A summary of all of the  $F$ -numbers obtained for this case is shown in Table IV.2. The table evidences the capability of this technique to prove the existence of the unsymmetrical ion-pairs as well as to differentiate the changes of the dissociation constants of these unsymmetrical ion-pairs.

Although Kurtze and Tamm's differential absorption data (see Fig. IV.9) were obtained at 20 °C and were expressed in  $\Delta\alpha/\alpha$ , no attempt was made to convert their data to that of 25 °C and in  $\Delta(\alpha\lambda)_m/(\alpha\lambda)_m$ , since the correction needed would be less than their measuring error. After having examined Fig. IV.9 it is fair to say that their  $F$ -number of .21 is good for  $[MgSO_4] = .1M$  at  $[NaCl]/[MgSO_4] = 1$  while our measured  $F$ -number is .14 for  $[MgSO_4] = .02M$  at  $[NaCl]/[MgSO_4] = 1$ . Thus, the acoustic data shows that the  $F$ -number is dependent upon not only the concentration ratio of the salts but also upon the initial magnesium sulfate concentration. A single  $F$ -number of .21 does not account for all the differential sound absorptions associated with magnesium sulfate solutions. The theoretical estimation of the  $MgSO_4^0$  ion-pair concentration supports this observation (see Fig. IV.9).

The addition of sodium chloride to the magnesium sulfate solution would also give rise to an increase in the sound speed<sup>81-85</sup> and to a reduction in the static compressibility<sup>81,86-88</sup> as well as to an increase in the viscosity<sup>89-91</sup> of the solution. The viscosity of the solution is one of the factors determining the classical sound absorption and hence the background correction base. The sound speed is required in converting the decay rate of the sound wave to sound absorption data. The static compressibility is one of the factors that determines the excess sound absorption. The sound speeds and the compressibilities of the solutions involved in this study are estimated and are given in Tables IV.3 and IV.4, respectively. A summary of the viscosity data from the literature is furnished in Table IV.5. After examination, the effect on the differential sound absorption due to the changes in these physical properties appeared to be



negligible for the solutions measured in this work.

The Debye-Hückel constants used for the activity coefficient computations are influenced by the dielectric property of the solution.<sup>11-13</sup> The dielectric constant in sodium chloride solution has been reported<sup>92</sup> to decrease with increasing sodium chloride concentration. An investigation based on this reported observation showed that the effect on  $MgSO_4$  ion-pair concentration due to the change in dielectric constant is not significant for the solutions measured in the research.

The validity of the activity coefficient equation used in this study was examined for the case of pure magnesium sulfate solutions. It was found that the total activity coefficients calculated were greater than those obtained by Pitzer<sup>51-54,93</sup> and Robinson and Stokes<sup>12</sup>, with increased differences up to 20 % by  $[MgSO_4] = .1M$ . Those calculated for  $.1M \leq [MgSO_4] \leq 1M$ , however, are close to the earliest freezing-point results<sup>94</sup> and to those of Robinson and Jones<sup>55</sup> and Lietzke and Stoughton<sup>58</sup> as well. In the paper by Wu, Rush and Scatchard,<sup>56</sup> Lietzke and Stoughton's values<sup>95</sup> were used in preference to those of Robinson and Stokes.<sup>12</sup> Robinson and Stokes normalized the values at .1M. Pitzer's values were obtained on the assumption of triplet ion associations and on the basis of Robinson and Stokes' values. Aware of these discrepancies, Culberson, Latham and Bates<sup>96</sup> used Pitzer's values in their paper in order to be internally consistent in comparison with the literature data.<sup>97</sup>

The extended Debye-Hückel equation has been used for solutions of higher ionic strength.<sup>21,37</sup> It was formulated by adding additional ionic strength dependent terms to the simple Debye-Hückel equation. It is still an empirical equation and is in need of some kind of basis for obtaining proper coefficients for the ionic strength dependent terms. For a .02M magnesium sulfate solution the difference caused by using the simple and the extended equations probably is minor. There is no evidence upon which to decide which equation is better. Further use of these equations for magnesium sulfate and sodium chloride mixture may encounter similar difficulties.

This study presented a model that demonstrated how sound absorption could be related to ion-pairing in solutions of magnesium sulfate and sodium chloride and how this technique works for the ion-pairing investigation. The model also forms the framework for an extended study for solutions of higher sodium chloride concentration and seawater; however, further improvement is needed due to the increased uncertainty of both the sound absorption theory and the ion-pair estimation method with increased addition of sodium chloride. The Eigen and Tamm's theory was initially devised for pure magnesium sulfate solution. It is not clear how the structures of the ion-pair concentrations and the partial volume of the species in the solution are affected by the considerable addition of sodium chloride. When a solution becomes concentrated not only the method of calculating the activity coefficients of the ions but also the effect on ion-pair activity have to be carefully considered. Although the sound absorption in .02M  $MgSO_4$  + .6M  $NaCl$  solution<sup>98</sup> and Lyman and Fleming seawater<sup>99,100</sup> have been recently measured at 25 °C and pressures up to 307 atm, at this early stage an attempt to explain these acoustic data is not included in this chapter.

Table IV.1  
 Summary of measured sound absorption data  
 and predicted  $MgSO_4^0$  ion-pair concentration  
 for solutions of  $[MgSO_4] = .02M$

$\frac{[NaCl]}{[MgSO_4]}$	0	1	2	4	6
$(\alpha\lambda)_m \times 10^6$	$80.75 \pm 0.55$	$71.55 \pm 1.14$	$61.50 \pm 1.13$	$52.85 \pm 0.58$	$45.35 \pm 0.53$
$F$	0	.129	.157	.132	.130
$\frac{\Delta(\alpha\lambda)_m}{(\alpha\lambda)_m}$	0	$.129 \pm .026$	$.313 \pm .034$	$.528 \pm .028$	$.781 \pm .033$
Predicted $[MgSO_4^0] \times 10^4 M$	77.78	68.62	61.36	50.27	42.10
Predicted $F$	0	.134	.134	.137	.141
Predicted $\frac{\Delta[MgSO_4^0]}{[MgSO_4^0]}$	0	.134	.268	.547	.848

Table IV.2  
Summary of  $F$ -numbers measured and predicted  
for solutions of  $[MgSO_4] = [NaCl] = .02M$

$K_{MgSO_4}$	$K_{NaSO_4^-}$	$K_{MgCl^+}$	$F$	REMARKS
			.21	Kurtze and Tamm
			.129	Measured in this work
.0062	.1	.178	.134	Predicted in this work
.0062	.2	.356	.093	Doubled dissociation constants of $NaSO_4^-$ and $MgCl^+$
.0062	100	100	.052	No $NaSO_4^-$ and $MgCl^+$
.0062	100	.178	.081	No $NaSO_4^-$
.0062	.1	100	.102	No $MgCl^+$

Table IV.3  
Speed of sound as a function of pressure at 25 °C

Pressure (atm)	1	71.1	123.5	184.7	188.1	245.9	307.1
(kg/cm <sup>2</sup> g)	0	72.42	126.55	189.83	193.35	253.11	316.3
(psig)	0	1030	1800	2700	2750	3600	4500
(bar g)	0	71.00	124.07	186.11	189.55	248.14	310.18
.02M $MgSO_4$	1499.58						1551.24
.02M $MgSO_4$ + .02M $NaCl$	1500.91						
.02M $MgSO_4$ + .04M $NaCl$	1502.25						
.02M $MgSO_4$ + .08M $NaCl$	1504.70						
.02M $MgSO_4$ + .12M $NaCl$	1507.18						
.02M $MgSO_4$ + .60M $NaCl$	1542.57						1587.26
.02M $NaCl$	1498.02						
.04M $NaCl$	1499.36						
.08M $NaCl$	1501.81						
.12M $NaCl$	1504.27						
.16M $NaCl$	1506.79						
.58M $NaCl$	1532.00	1542.90	1551.80	1562.23	1562.80	1572.55	1582.84
.60M $NaCl$	1539.68						1583.98
.03M $Na_2SO_4$	1501.72						
Water	1496.69	1508.63	1517.56	1528.00	1528.58	1538.44	1548.88
Seawater	1533.80	1545.79	1554.57	1564.90	1565.47	1575.30	1585.76

Table IV.4  
Static compressibility ( $10^{-6} \text{ bar}^{-1}$ ) at 25 °C and 1 atm

SOLUTION	PRESSURE(atm)	$\beta_s$	$\beta$
Water	1	44.7	45.2
	307	41.2	41.86
Seawater	1	41.55	42.19
	307	38.5	
.02M $\text{MgSO}_4$	1	44.5	
	307	41.0	
.02M NaCl	1	44.66	
.04M NaCl	1	44.55	
.08M NaCl	1	44.33	
.12M NaCl	1	44.11	
.60M NaCl	1	41.65	
.02M $\text{MgSO}_4$ + .02M NaCl	1	44.48	
.02M $\text{MgSO}_4$ + .04M NaCl	1	44.37	
.02M $\text{MgSO}_4$ + .08M NaCl	1	44.15	
.02M $\text{MgSO}_4$ + .12M NaCl	1	43.93	
.02M $\text{MgSO}_4$ + .60M NaCl	1	41.47	
	307	38.37	

Table IV.5  
Ratio of the viscosity in solutions to that in water at 25 °C

SOLUTION	PRESSURE	$\eta/\eta_w$
Water	300 atm	1.1
.16M NaCl	1 atm	1.02
.60M NaCl	1 atm	1.06
.02M $\text{MgSO}_4$	1 atm	1.02
Seawater	1 atm	1.11
.50M NaCl	5000 psi	0.99

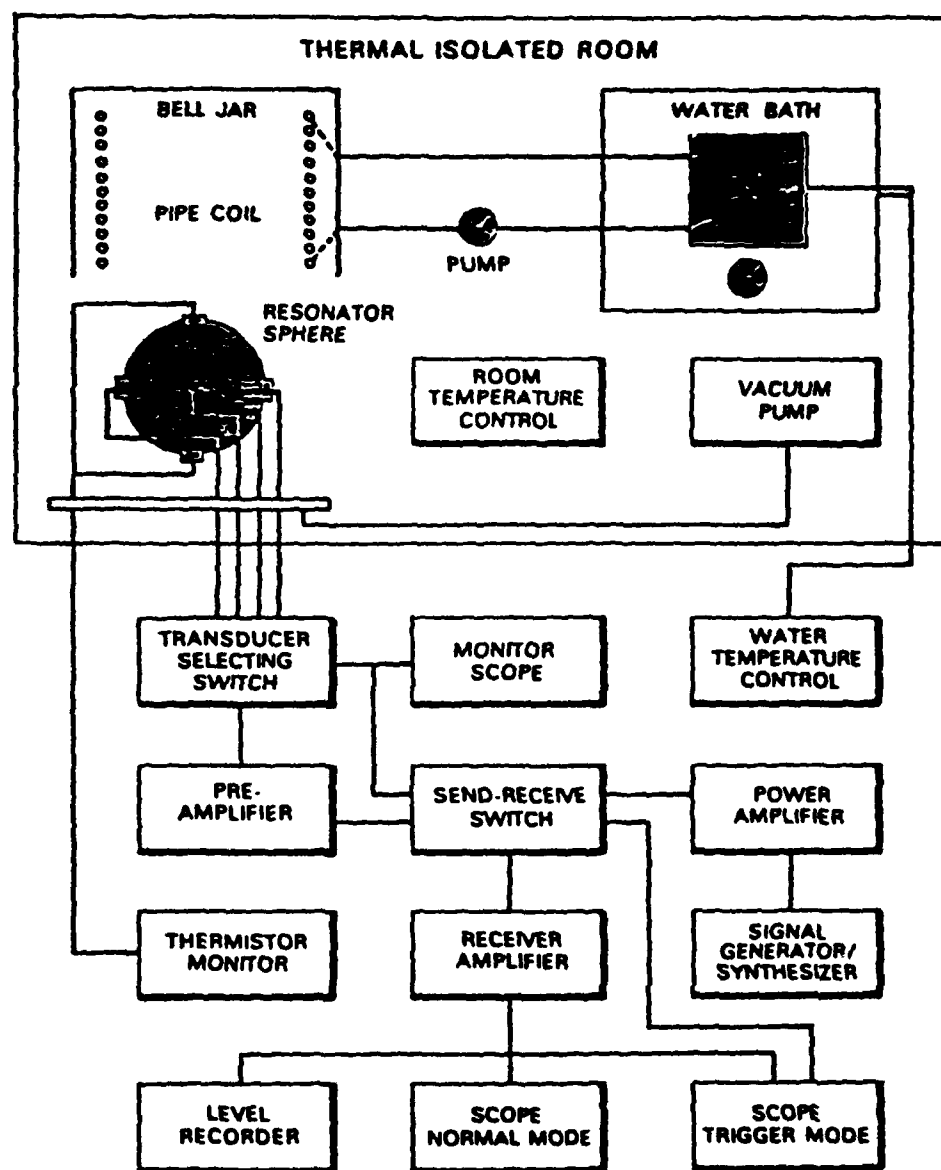


Figure IV.1 Block diagram of the measuring apparatus.

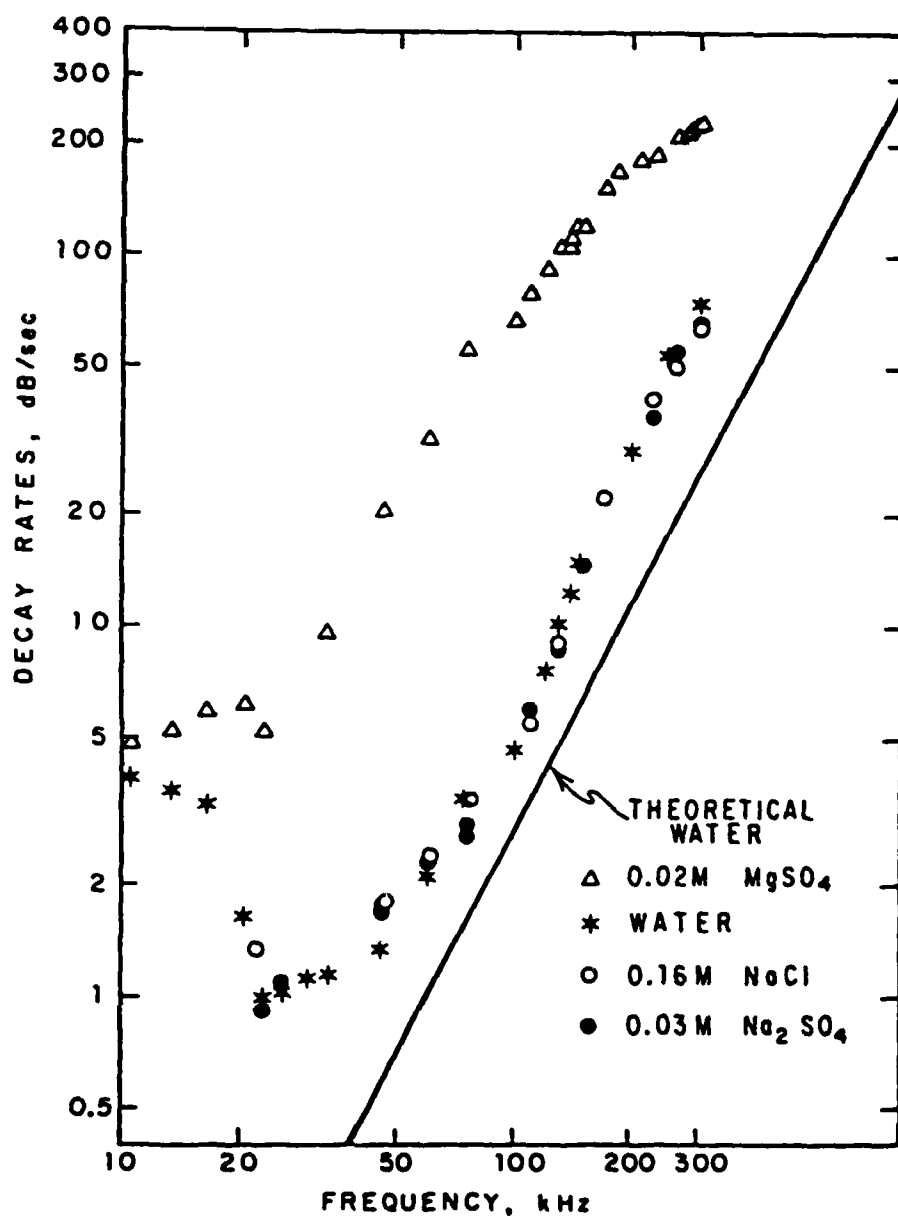


Figure IV.2 Measured decay rates of sound waves in water, .02M magnesium sulfate, .16M sodium chloride and .03M sodium sulfate solutions.



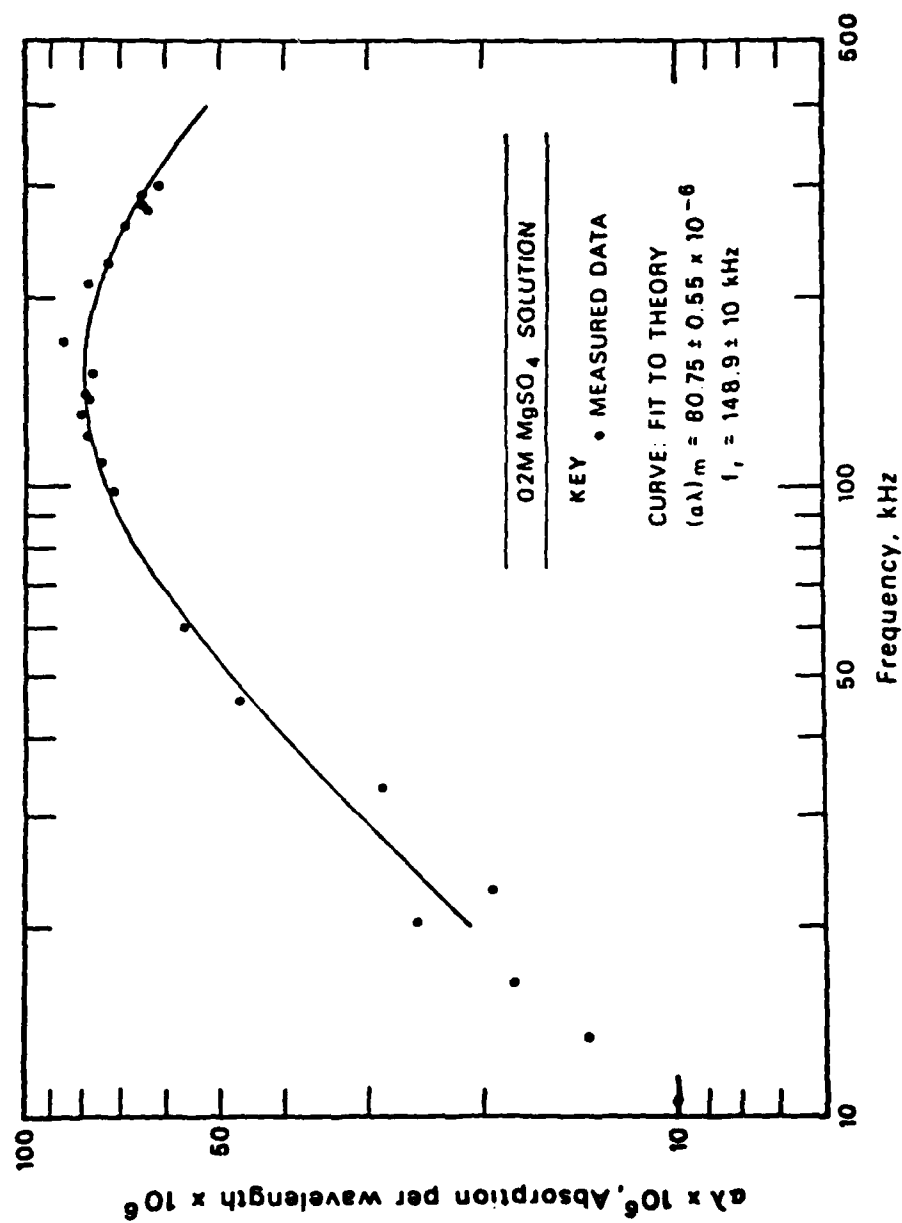


Figure IV.3 Measured sound absorption data and theoretically fitted curve for 0.02M magnesium sulfate solution.

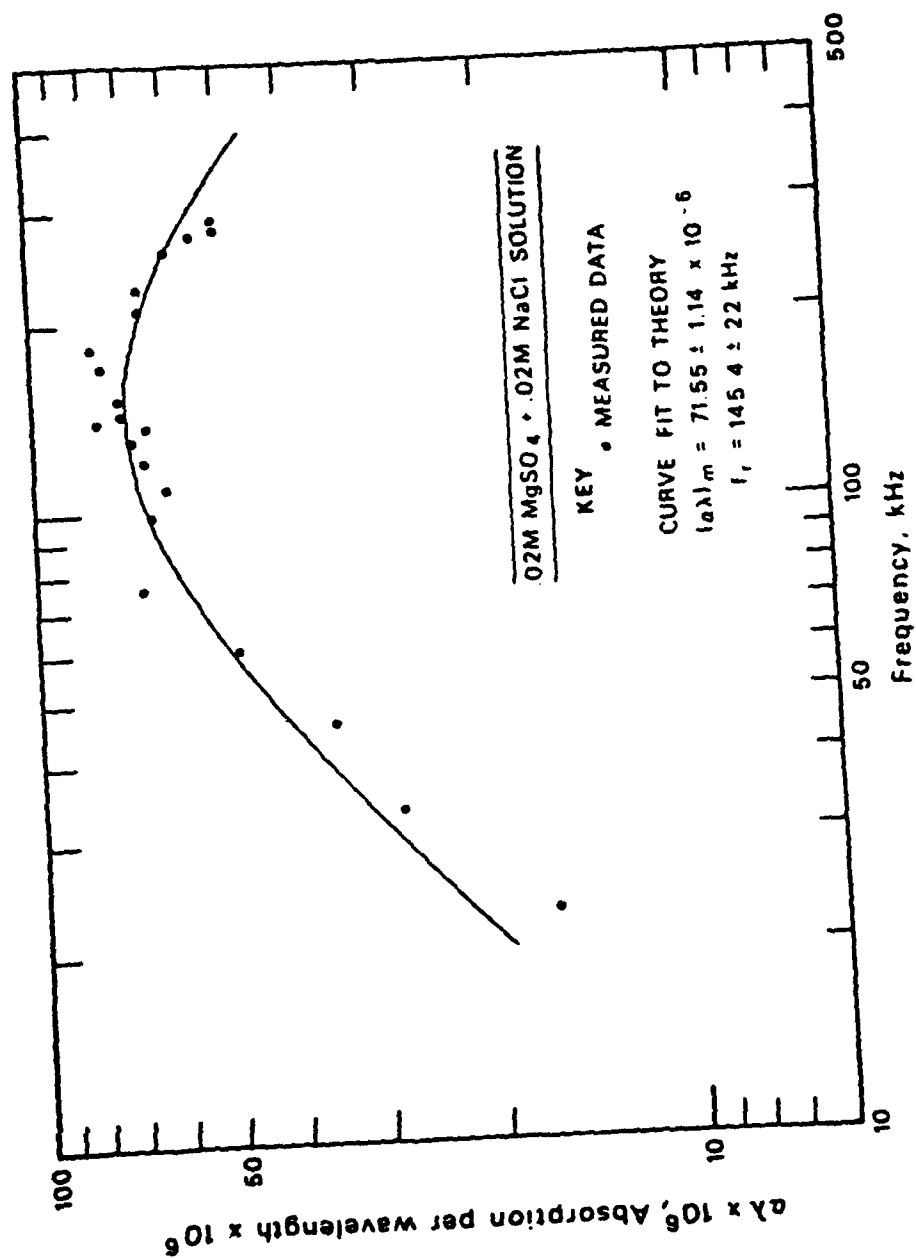


Figure IV.4 Measured sound absorption data and theoretically fitted curve for .02M magnesium sulfate and .02M sodium chloride mixture.

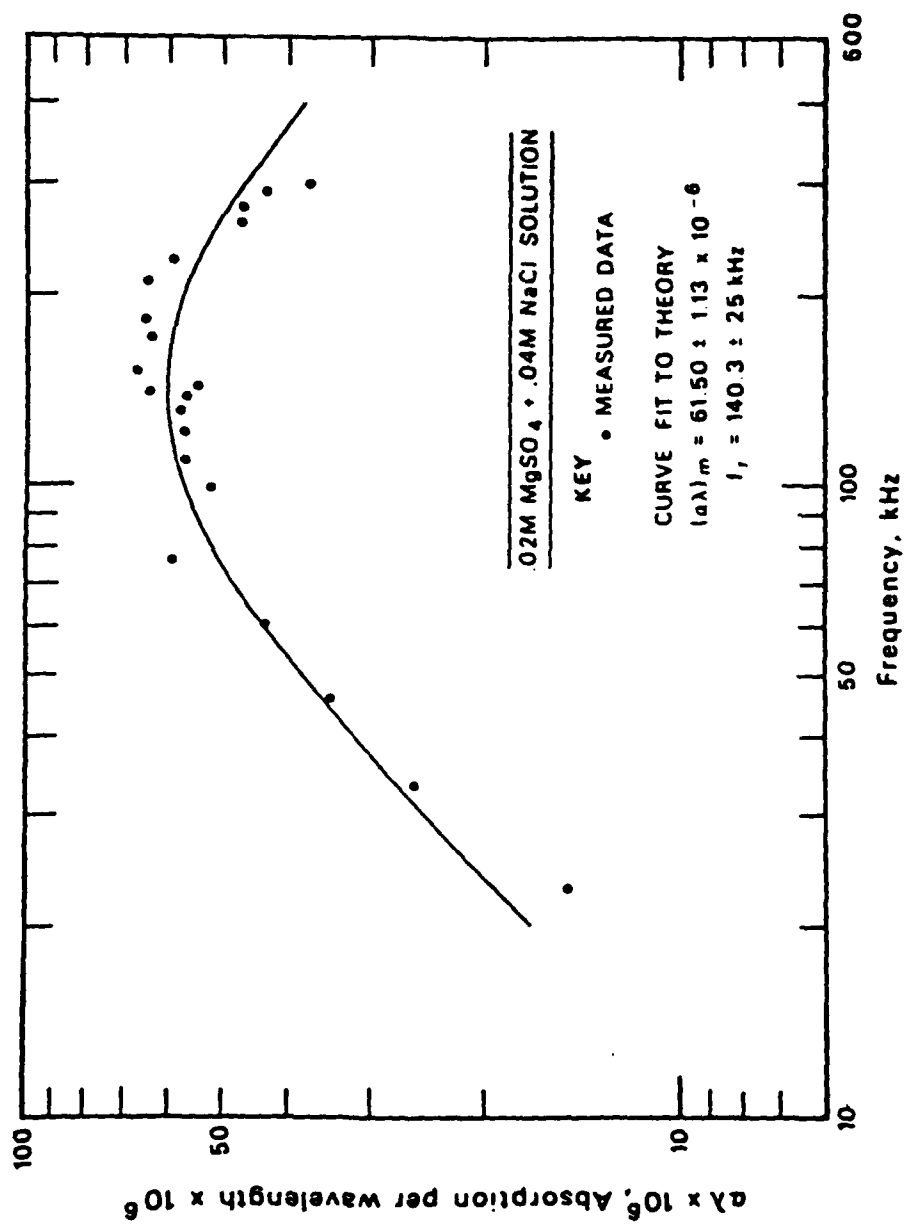


Figure IV.5 Measured sound absorption data and theoretically fitted curve for .02M magnesium sulfate and .04M sodium chloride mixture.

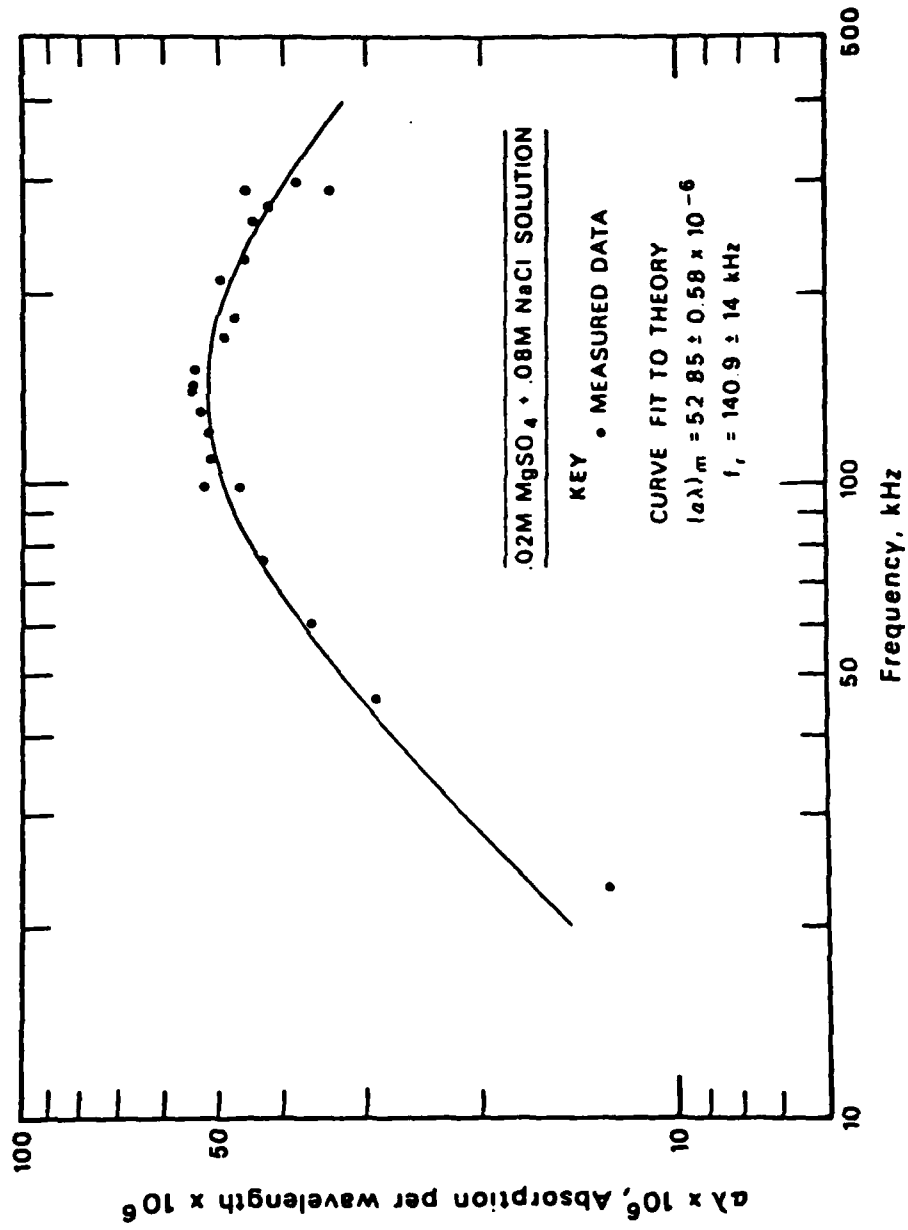
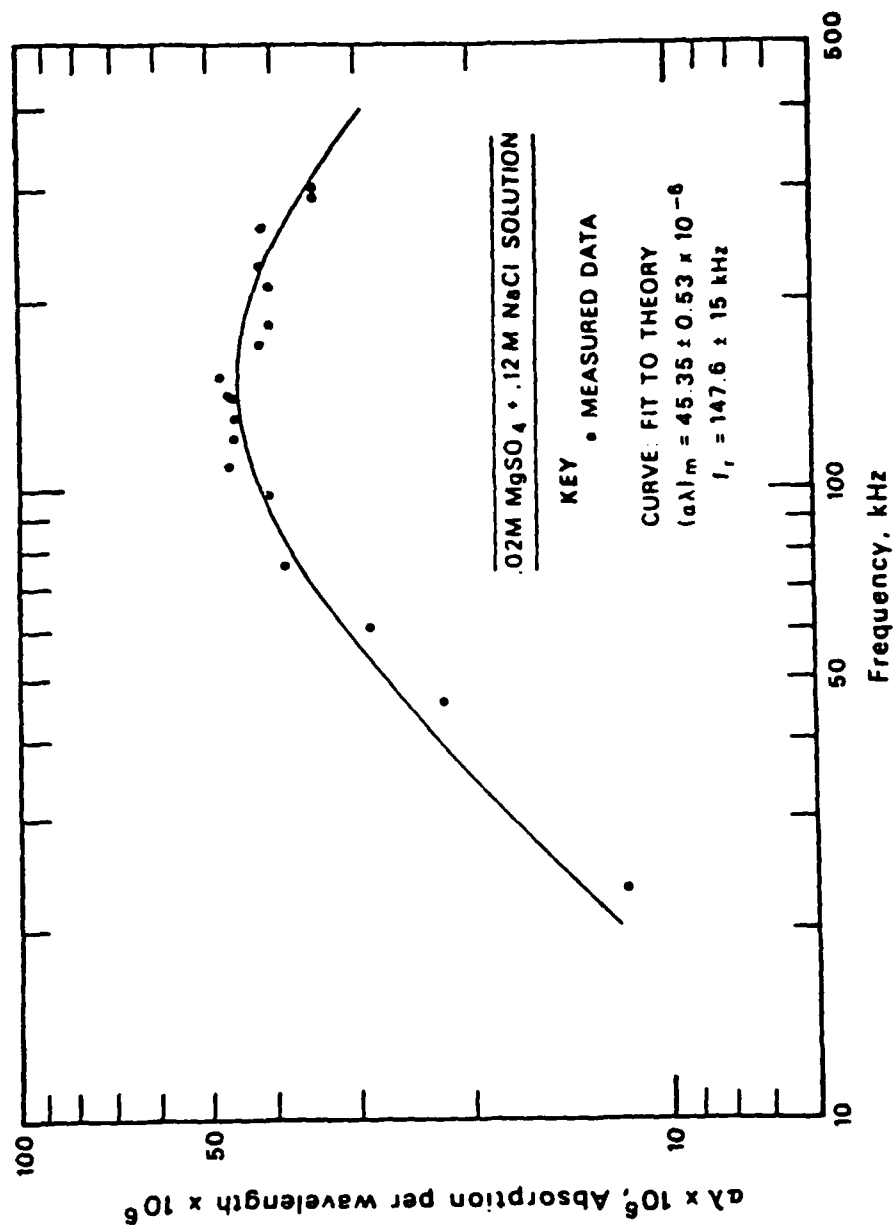


Figure IV.6 Measured sound absorption data and theoretically fitted curve for .02M magnesium sulfate and .08M sodium chloride mixture.



**Figure IV.7** Measured sound absorption data and theoretically fitted curve for .02M magnesium sulfate and .12M sodium chloride mixture.

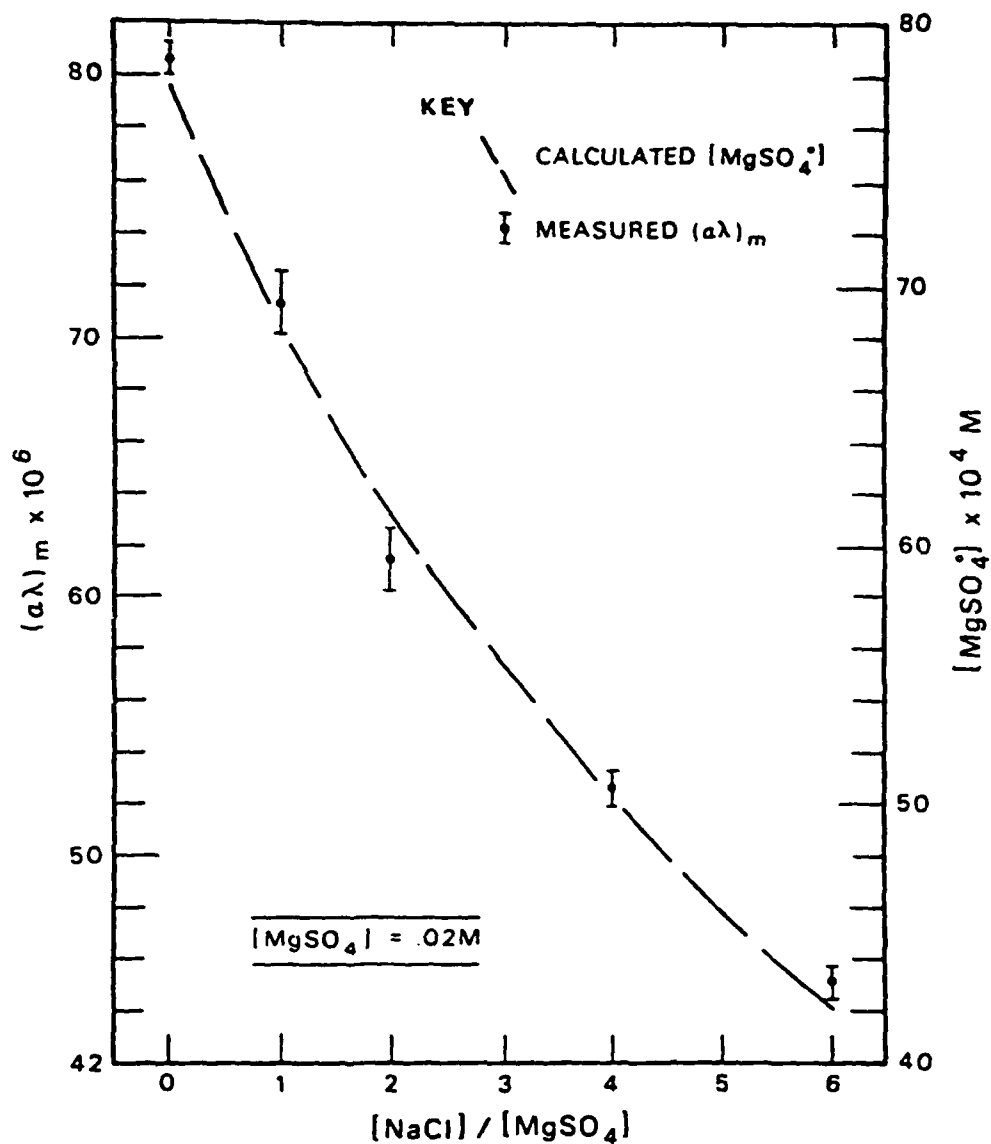


Figure IV.8 Measured sound absorption data versus predicted magnesium sulfate ion-pair concentrations.

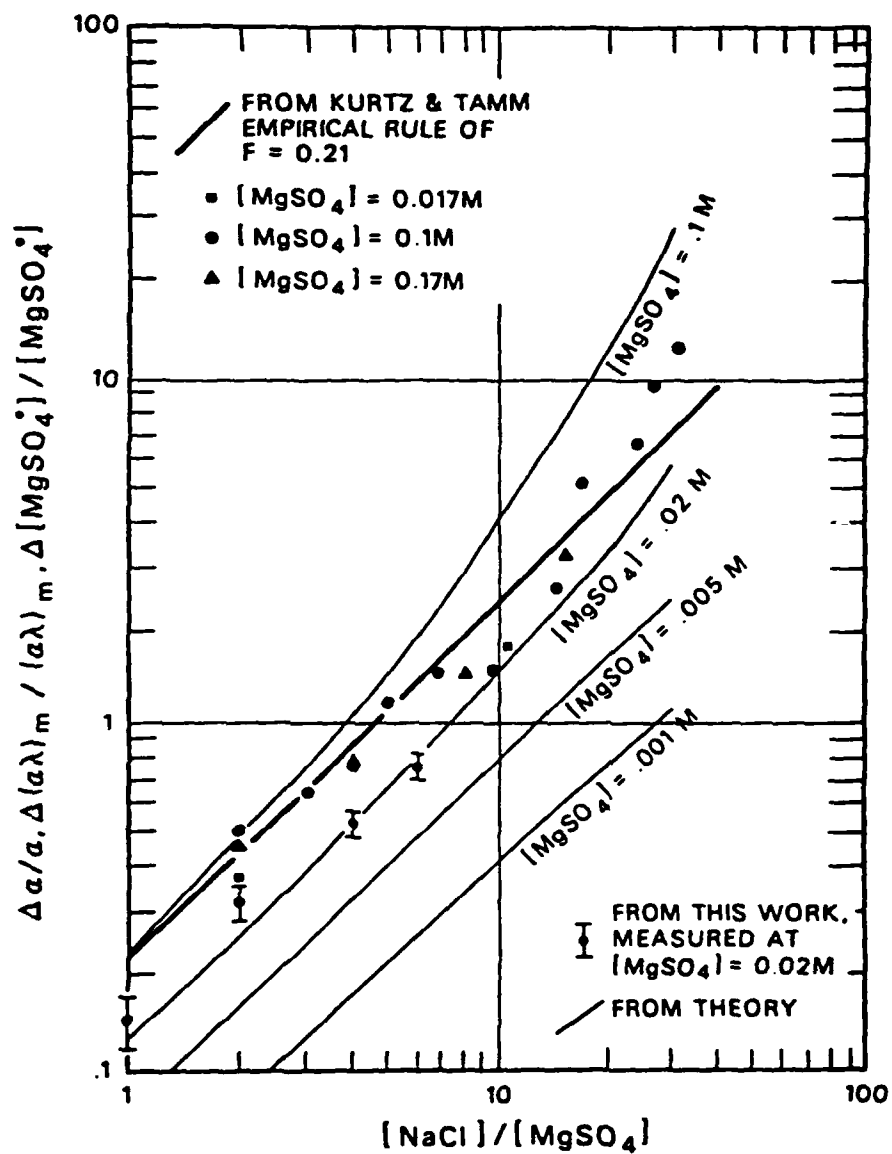


Figure IV.9 Measured differential sound absorption and predicted differential magnesium sulfate ion-pair concentration and Kurtze and Tamm's results.

## V. PRESSURE EFFECT ON SOUND ABSORPTION IN SEAWATER AND RELAXATIONAL ABSORPTION WITH MAGNESIUM SULFATE

### A. Introduction

Leonard, Combs and Skidmore<sup>106</sup> found that magnesium sulfate is responsible for the excess sound absorption in the 100 KHz region in seawater. In the same frequency region other seawater salts do not show significant excess absorption. Liebermann<sup>1</sup> demonstrated that the sound absorption in magnesium sulphate solution as well as in seawater can be accounted for by the pressure-dependent relaxation process associated with the equilibrium of magnesium sulfate. Wilson and Leonard<sup>80</sup> investigated the relaxational sound absorption process in magnesium sulfate solution and seawater at 1 atm and different temperatures and found that the sound absorption in seawater is equivalent to that in a .014M magnesium sulfate solution.<sup>3</sup> Besides the primary relaxation process which occurs in the 100 KHz region, Kurtze and Tamm<sup>3</sup> also observed other processes in magnesium sulfate solutions in the MHz region. Eigen and Tamm<sup>10</sup> proposed a 4-state association model for magnesium sulfate equilibrium and derived a sound absorption theory on the basis of this model. This sound absorption theory provides a quantitative explanation of Kurtze and Tamm's<sup>3</sup> acoustic data at atmospheric pressure. Fisher<sup>73</sup> showed that this theory provides a basis for explaining the pressure dependence of acoustic and conductance data in magnesium sulfate solutions. However, there some discrepancies<sup>17,62-68,114</sup> remain regarding complete quantitative agreement.

The investigation of a relaxational sound absorption process necessitates adequate absorption data in a range of frequency which is able to cover the neighborhood of the relaxation frequency. Therefore, although many measurements<sup>109</sup> relevant to the sound absorption in seawater have been made in the sea and in laboratories, very few<sup>80,110,117</sup> were able to provide reliable data for a relaxational sound absorption study, primarily due to the limited frequencies chosen for the studies and the varied situations encountered in the sea.



From all available data and theories Schulkin and Marsh<sup>109</sup> derived an expression in terms of salinity, temperature and pressure for calculations of sound absorption in seawater. In this expression the relaxation dependence and the pressure effect were, however, based largely on the results from the magnesium sulfate solutions due to the paucity of information in these two areas. Fisher and Simmons,<sup>106</sup> later, presented an equation for the sound absorption in seawater which included Simmons'<sup>117</sup> experimental data of boric acid relaxation in seawater and renewed pressure effects in magnesium sulfate solution and in pure water.<sup>106</sup> Again, as in the Schulkin and Marsh's<sup>109</sup> equation, the pressure effect obtained for a .5M magnesium sulfate solution was the only information available at that time. Schulkin and Marsh<sup>109</sup> later discussed the sound absorption due to the boric acid relaxation in seawater according to Simmons'<sup>117</sup> data.

Relaxational sound absorption due to the boric acid is centered in the vicinity of 1 KHz. Between this frequency and the frequency of the primary relaxation due to magnesium sulfate another relaxation absorption due to the magnesium carbonate is recently reported by Mellen, Browning and Simmons.<sup>112,113</sup> Both boric acid and magnesium carbonate relaxations are found to be highly pH-dependent.<sup>111</sup> The one with magnesium sulfate, however, is nearly independent of pH in seawater.<sup>111</sup>

The pressure effect on sound absorption in pure water has been measured at frequencies of 25 and 45 MHz by Litovitz and Carnevale.<sup>118</sup> Their data showed a 12-13% reduction of the decay rate of sound wave for a pressure change from 1 to 500 Kg/cm<sup>2</sup>. Fisher<sup>73,104,119</sup> studied the pressure effect on sound absorption at 100 and 500 KHz for .5M  $MgSO_4$  solution and observed a 60% reduction on sound absorption for a pressure change from 1 to 1000 atm. No appreciable shift of relaxation frequency was found. Bezdek<sup>110</sup> made measurements in the Pacific Ocean using 6 different frequency signals in 30-145 kHz. Based on the data gathered at depths of 200, 1000, 2000 and 2800 m at temperatures of approximately 7°, 3.5°, 3° and 2.5°C, respectively, he obtained a pressure factor of  $12-14 \times 10^{-4}/\text{atm}$  for a frequency range of 50-150 KHz and observed an increase in the relaxation frequency with increased depth. Simmons<sup>117</sup>

measured the sound absorption for Lyman and Fleming<sup>100</sup> seawater at 1 atm and various temperatures using a 200-liter spherical resonator.

For both seawater and magnesium sulfate solutions, the results from the aforementioned investigations showed decreases in both the relaxation frequency and the maximum absorption with decreasing temperature. For magnesium sulfate solutions, the magnitude of the relaxation absorption due to magnesium sulfate equilibrium is affected by both the temperature and the pressure changes. There are more decreases of the magnitude with increased pressure and less decreases with decreased temperature. The relaxation frequency is likely to be affected only by the temperature change; it shifts to lower frequencies with decreasing temperature. For seawater, the pressure and temperature effects on the magnitude of the absorption are comparable to that in magnesium sulfate. However, the relaxation frequency seems to be complicated for some reasons. These reasons are obviously closely tied to the existence of other salts in seawater although how they affect the relaxation process in seawater in the 100 KHz region, which is dominated by the magnesium sulfate, is unclear. If Bezdek's<sup>110</sup> data is correct the relaxation frequency expression in Schulkin and Marsh<sup>109</sup> equation should be a function of both temperature and pressure. Recently, Mellen, Browning and Simmons<sup>112,113</sup> have investigated the sound absorption in seawater due to equilibria of various ion-pairs and showed theoretically that the coupling of two equilibria through common ions could cause a shift in relaxation frequency.

Measurements of the pressure effect on magnesium sulfate equilibrium have been made by Fisher<sup>73,104,105,119</sup> and Fisher and Fox.<sup>17</sup> From these measurements the volume changes of the species in the solution were obtained. The volume change data is related to the excess sound absorption as well as to the physical structure of the magnesium sulfate equilibrium in solution.<sup>10</sup> An investigation of how volume change data is affected by the addition of sodium chloride as well as other salts in seawater would make a valuable study.

Pressure measurements on sound absorption can be made for seawater and for the

mixture of magnesium sulfate and sodium chloride. Considering only the dominant relaxational absorption process in the frequency range of 30 to 300 KHz which is due to the magnesium sulfate equilibrium, the pressure effect on magnesium sulfate equilibrium in those solutions can be analyzed by utilizing these measurement results. The addition of sodium chloride to a magnesium sulfate solution itself does not add extra absorption but does change the physical properties of the solutions which are related to the excess sound absorption due to magnesium sulfate equilibrium.

### B. Measurements, Results and Discussions

Sound absorption measurements were made for .02M magnesium sulfate solution,<sup>98</sup> .02M magnesium sulfate and .6M sodium chloride mixture<sup>98</sup> and Lyman and Fleming seawater<sup>99</sup> at 25 °C and pressures up to 307 atm using the spherical resonator method. The measuring technique has been described before. Solutions were prepared from AR-rated reagents and deionized water and were degassed.

The measured relaxational absorption data and their least-square -root fitted curves are shown in Fig. V.1 to Fig. V.8. Absorption data and the curve fitting results are given in Appendix D. The results of the maximum absorption,  $(\alpha\lambda)_m$ , and the relaxation frequency,  $f_r$ , obtained from the curve fitting program, are summarized in Table V.1. No significant shift of relaxation frequency was found for these solutions. This observation agrees with Fisher's<sup>73,119</sup> result for magnesium sulfate solution, but not with Bezdek's<sup>110</sup> result for seawater.

Assuming the magnitude of sound absorption is linearly dependent on the pressure in the range of 1 to 307 atm, the pressure factor,  $b$ , was calculated from following equation

$$\frac{(\alpha\lambda)_m(P)}{(\alpha\lambda)_m(0)} = 1 + bP \quad (V.1)$$

where  $(\alpha\lambda)_m(P)$  is the maximum absorption per wavelength in neper obtained at pressure of  $P$  atm.g and  $(\alpha\lambda)_m(0)$  is that at atmospheric pressure and  $b$  is in atm.g<sup>-1</sup>. The pressure factors thus calculated are summarized in Table V.2, where those from previous investigations are also

shown for a comparison. From these results a plot of the pressure effect in terms of Eq. (V.1) is obtained as shown in Fig. V.9. These results show a tendency toward an increasing pressure effect for solutions changing from the pure magnesium sulfate, through the mixture of magnesium sulfate and sodium chloride, to seawater.

The total reduction on maximum absorption at 307 atm is summarized in Table V.3. The magnesium sulfate solution and the mixture of magnesium sulfate and sodium chloride show a comparable pressure effect, which is different from the seawater result. This indicates that the addition of sodium chloride up to an ionic strength of seawater likely does not produce a significant effect on the volume change or the reaction rates associated with the primary relaxation of the magnesium sulfate equilibrium. The greater pressure effect on sound absorption in seawater suggested less available  $MgSO_4$  ion-pairs at high pressure for seawater than for magnesium sulfate solution and mixture. Possibly this is due to interactions between magnesium sulfate and other salts in seawater or to the indirect pressure effect of other salts in seawater.

Another examination considered the sound absorption reduction at the same pressure. The equivalent pure magnesium sulfate concentration for the mixture and seawater are summarized in Table V.4. It shows that the pressure effect on maximum absorption due to the sodium chloride in mixture is the same whether at 1 atm or at 307 atm as is that due to the other salts in seawater.

The results of the maximum absorption in seawater measured at 1 atm are summarized in Table V.5 and plotted in Fig. V.10. Below 25 °C, large discrepancies are noticed between the results predicted by Schulkin and Marsh's equation and those measured by other investigators. These measured data were obtained in laboratories at 1 atm which differs from the actual seawater situation. Thus, detailed analysis is needed to explain the discrepancies.

Data on the relaxation frequency obtained from the measurements for seawater at different temperatures are summarized in Table V.6 and plotted in Fig. V.11. Agreement is generally obtained. Schulkin and Marsh's expression of relaxation frequency is supported by

the experiment results.

Table V.1  
Results of maximum absorption and relaxation frequency  
at 25 °C

P (atmg)	$(\alpha\lambda)_m \times 10^6$	$f_r$ (KHz)	SOLUTION
0	61.30 ± .46	140.3 ± 11.	Lyman and Fleming seawater
70	57.75 ± .54	139.9 ± 11.	
187	52.90 ± .34	133.4 ± 8.	
306	45.20 ± .32	142.1 ± 7.	
0	80.75 ± .55	148.9 ± 10.	.02M $MgSO_4$
306	64.95 ± .43	145.1 ± 8.	
0	20.20 ± .32	162.3 ± 20.	.02M $MgSO_4$ + .6M NaCl
306	16.20 ± .24	150.8 ± 14.	

Table V.2  
Summary of pressure effect  
on maximum excess sound absorption at 25 °C

INVESTIGATOR	$-b_1 \times 10^4$	$b_2 \times 10^8$
Hsu and Fisher (.02M $MgSO_4$ )	6.39 ± .35	0
Hsu and Fisher (.02M $MgSO_4$ + .6M NaCl)	6.47 ± .81	0
Hsu and Fisher (Seawater)	8.06 ± 1.08	0
Schulkin and Marsh (Seawater) <sup>109</sup>	6.54	0
Bezdek (Seawater <i>in situ</i> ) <sup>110</sup>	12.90	0
Fisher (.5M $MgSO_4$ ) <sup>106</sup>	10.30	37.00
Litovitz and Carnevale (Water 30 °C) <sup>118</sup>	3.84	7.57

$$\frac{(\alpha\lambda)_m(P)}{(\alpha\lambda)_m(0)} = 1 + b_1 P, \quad \text{for Hsu and Fisher}$$

$$\frac{\alpha(P)}{\alpha(0)} = 1 + b_1 P + b_2 P^2, \quad \text{for others}$$

**Table V.3**  
**Percentage reduction of maximum absorption with pressure**

SOLUTION	1 atm	307 atm	PERCENTAGE REDUCTION (%)
.02M $MgSO_4$	$80.75 \times 10^{-6}$	$64.95 \times 10^{-6}$	19.6
.02M $MgSO_4$ + .6M $NaCl$	$20.2 \times 10^{-6}$	$16.2 \times 10^{-6}$	19.8
Seawater	$61.3 \times 10^{-6}$	$45.2 \times 10^{-6}$	26.3

**Table V.4**  
**Equivalent magnesium sulfate concentration in mixture and seawater**

SOLUTION	1 atm	307 atm	EQUIVALENT CONCENTRATION
.02M $MgSO_4$	$80.75 \times 10^{-6}$	$64.95 \times 10^{-6}$	.02M
.02M $MgSO_4$ + .6M $NaCl$	$20.2 \times 10^{-6}$	$16.2 \times 10^{-6}$	.005M
Seawater	$61.3 \times 10^{-6}$	$45.2 \times 10^{-6}$	.015M

Table V.5  
Maximum excess sound absorption in seawater at 1 atm

T (°C)	$(\alpha\lambda)_m \times 10^6$	SOURCE
5.1	41.0 <sup>a</sup>	Wilson & Leonard <sup>80</sup>
15.0	44.0 <sup>a</sup>	a. Natural Seawater b. Synthesized Seawater
22.5	52.0 <sup>a,b</sup>	
0.0	58.5	Schulkin & Marsh <sup>109</sup> Theoretical
5.0	59.3	See equations below S = 34.5 per thousand A = $2.34 \times 10^{-6}$ v = sound speed
10.0	60.1	
15.0	60.8	
20.0	61.4	
25.0	61.9	
30.0	62.4	
35.0	62.8	
40.0	63.1	
4.0	45.0	Simmons <sup>117</sup> Lyman & Fleming Seawater
9.0	43.0	
20.0	57.0	
28.5	61.0	
36.0	63.0	
25.0	61.30 ± .46	Hsu & Fisher Lyman & Fleming Seawater

$$\alpha = \frac{SAf_r f^2}{f_r^2 + f^2} \text{ m}^{-1} \quad (\alpha\lambda)_m = SA\nu/2$$



**Table V.6**  
**Relaxation frequency of sound absorption process**  
**in seawater at 1 atm**

T (°C)	$f_r$ (KHz)	SOURCE
5.1	60.0 <sup>a</sup>	Wilson & Leonard <sup>80</sup>
15.0	120.0 <sup>a</sup>	a. Natural Seawater b. Synthesized Seawater
22.5	190.0 <sup>a,b</sup>	
0.0	59.2	Schulkin & Marsh <sup>109</sup>
5.0	74.6	Theoretical
10.0	93.2	See equation below
15.0	115.5	T in °C
20.0	142.1	
25.0	173.7	
30.0	210.8	
35.0	254.3	
40.0	304.9	
4.0	69.0	Simmons <sup>117</sup>
9.0	86.0	Lyman & Fleming Seawater
20.0	145.0	
28.5	185.0	
36.0	240.0	
25.0	140.3	Hsu & Fisher
		Lyman & Fleming Seawater

$$f_r = 21.9 \times 10^{[6-1520/(T+273)]} \text{ KHz}$$

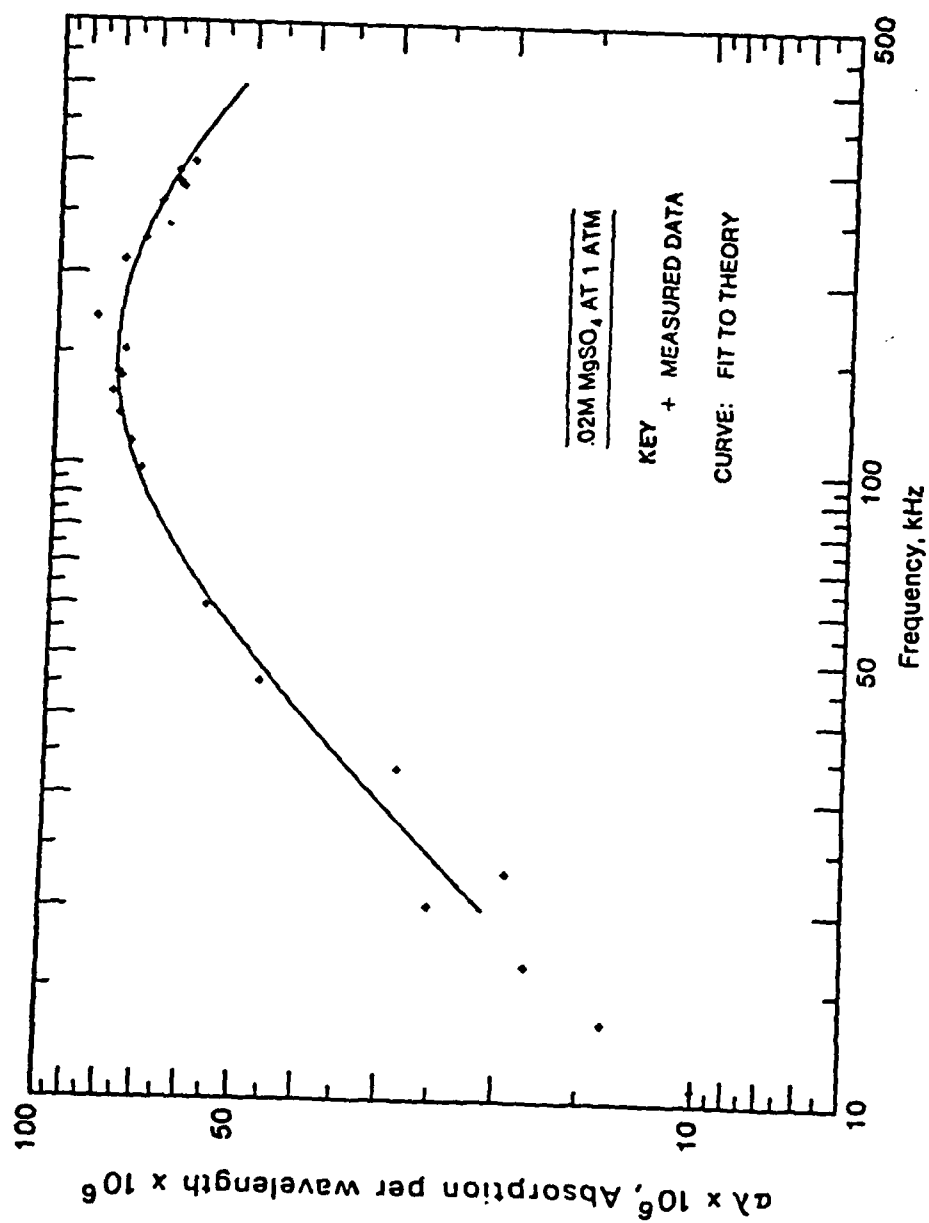


Figure V.1 Measured sound absorption data and theoretically fitted curve for .02M magnesium sulfate solution at 1 atm.

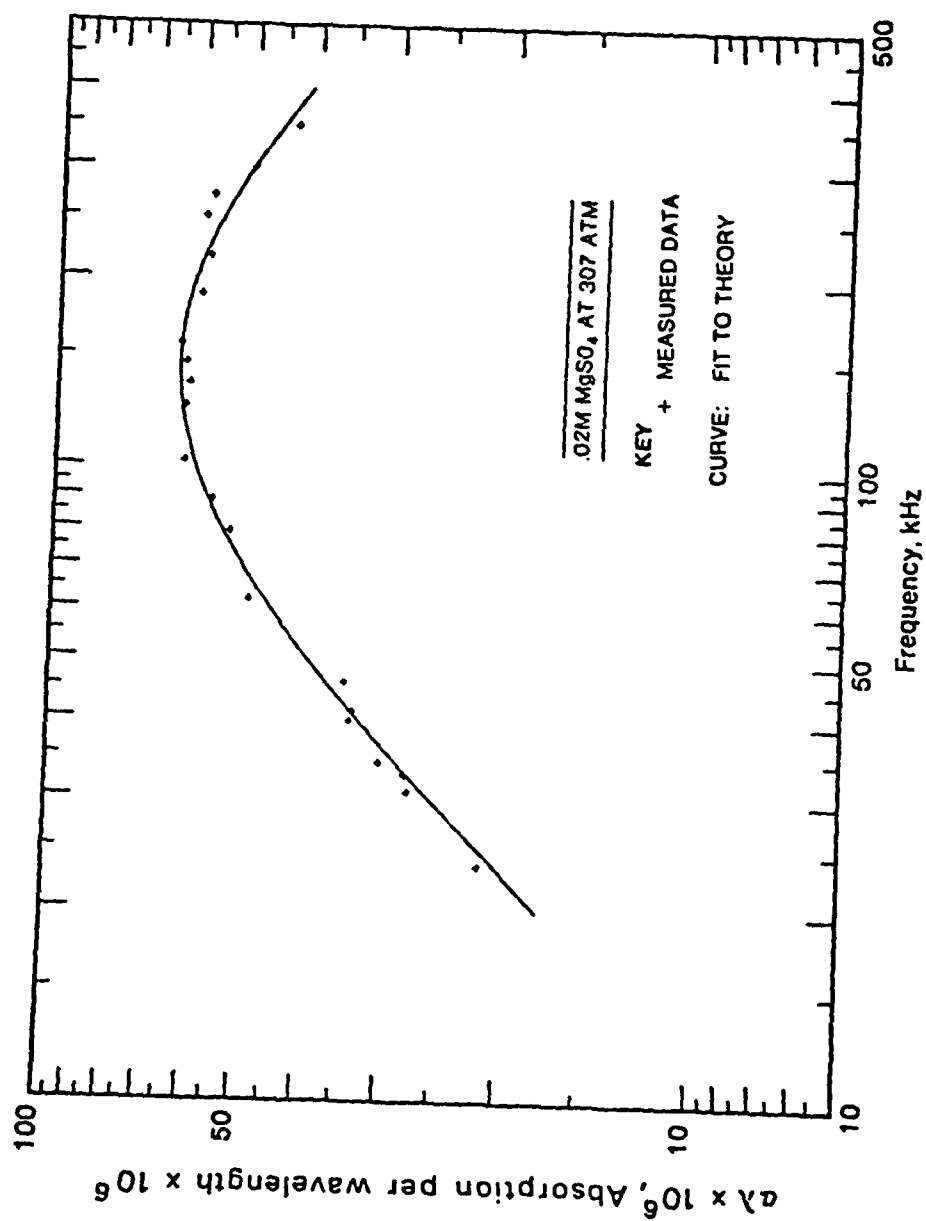


Figure V.2 Measured sound absorption data and theoretically fitted curve for .02M magnesium sulfate solution at 307 atm.

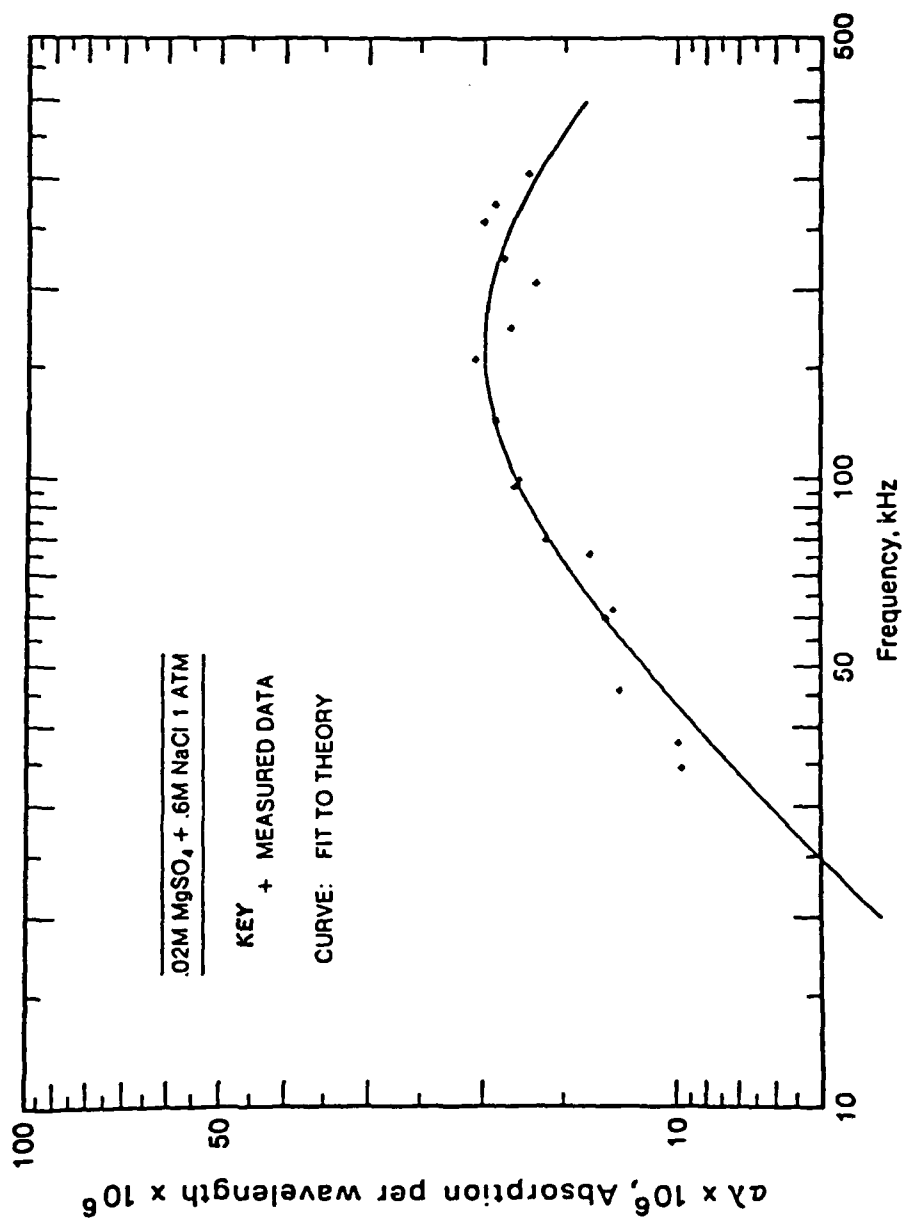


Figure V.3 Measured sound absorption data and theoretically fitted curve for  
 .02M magnesium sulfate and .6M sodium chloride mixture at 1 atm.

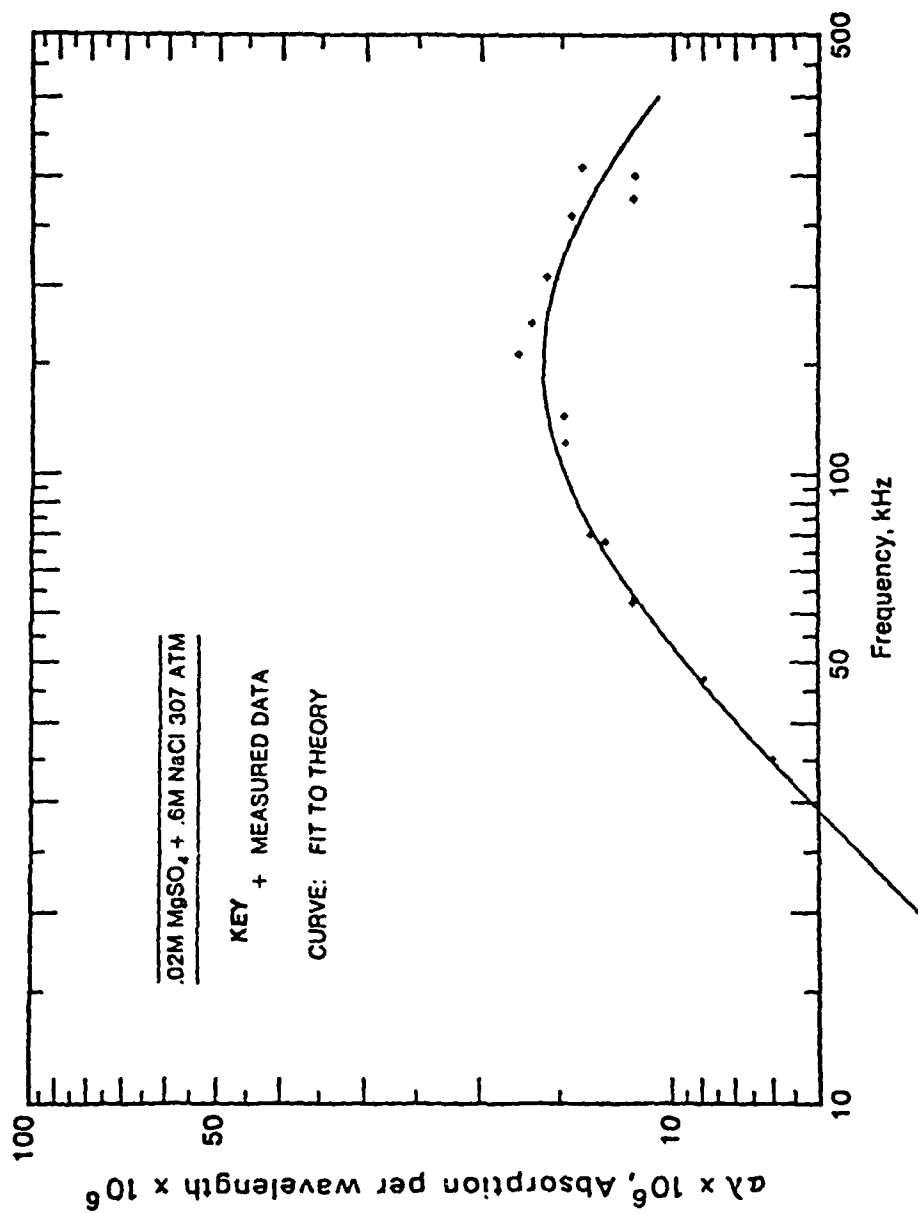


Figure V.4 Measured sound absorption data and theoretically fitted curve for .02M magnesium sulfate and .6M sodium chloride mixture at 307 atm.

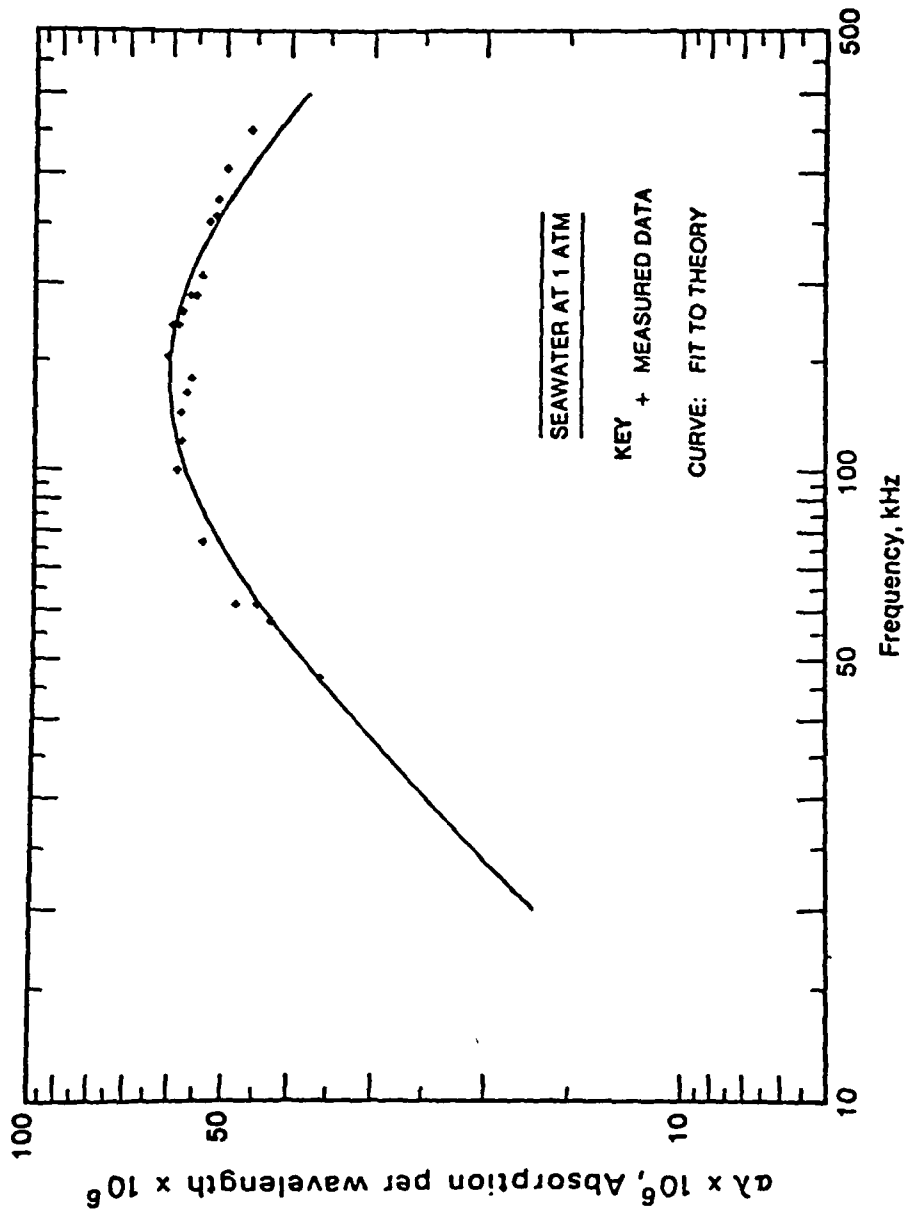


Figure V.5 Measured sound absorption data and theoretically fitted curve for Lyman and Fleming seawater at 1 atm.

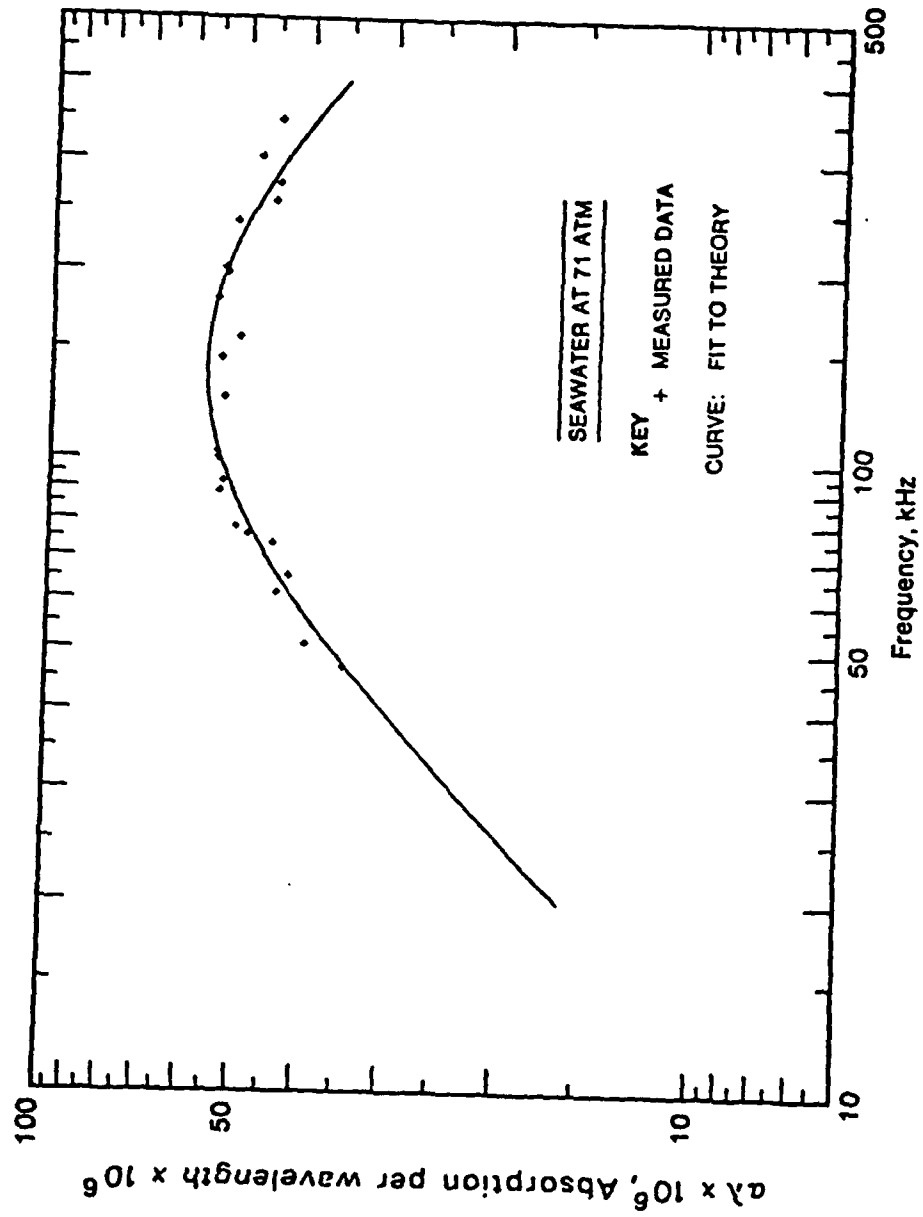


Figure V.6 Measured sound absorption data and theoretically fitted curve for Lyman and Fleming seawater at 71 atm.

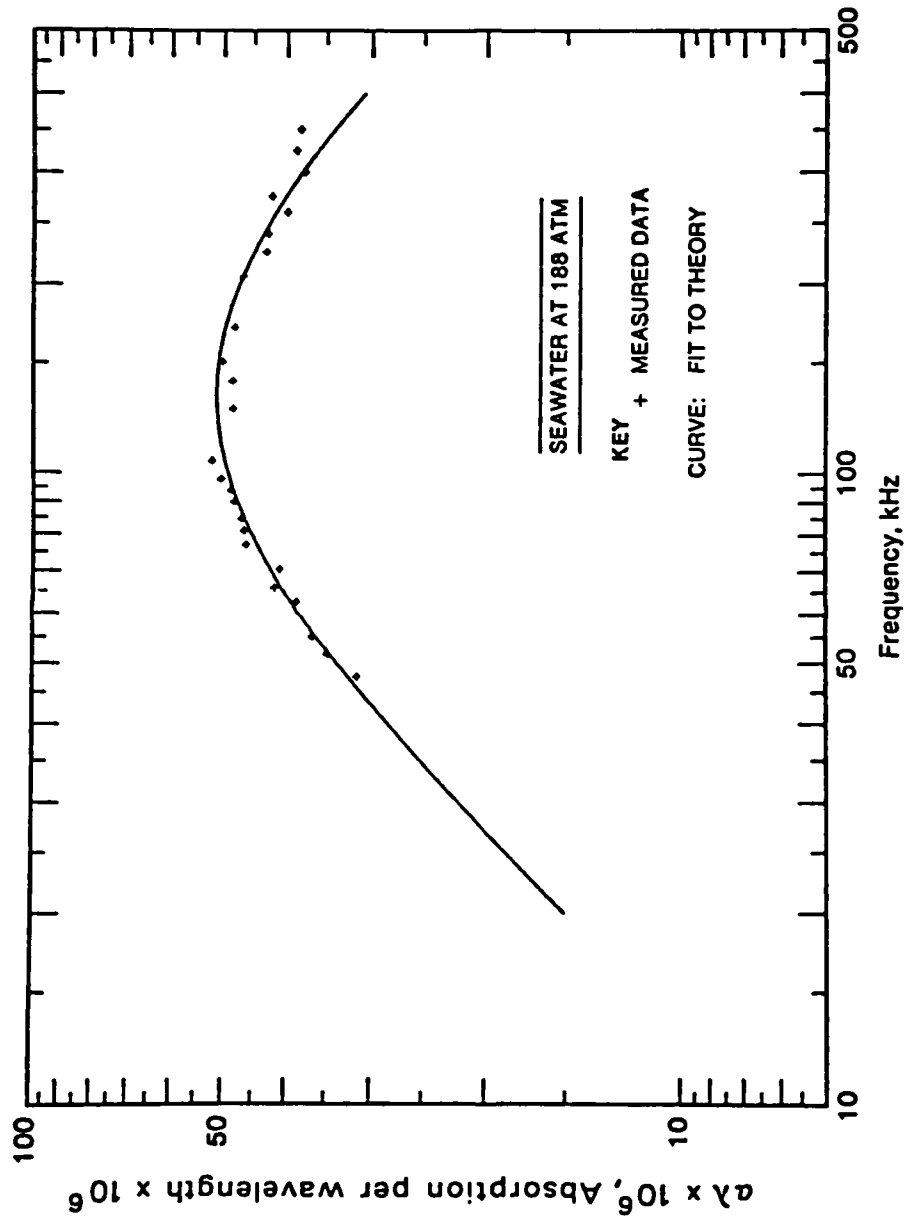


Figure V.7 Measured sound absorption data and theoretically fitted curve for Lyman and Fleming seawater at 188 atm.



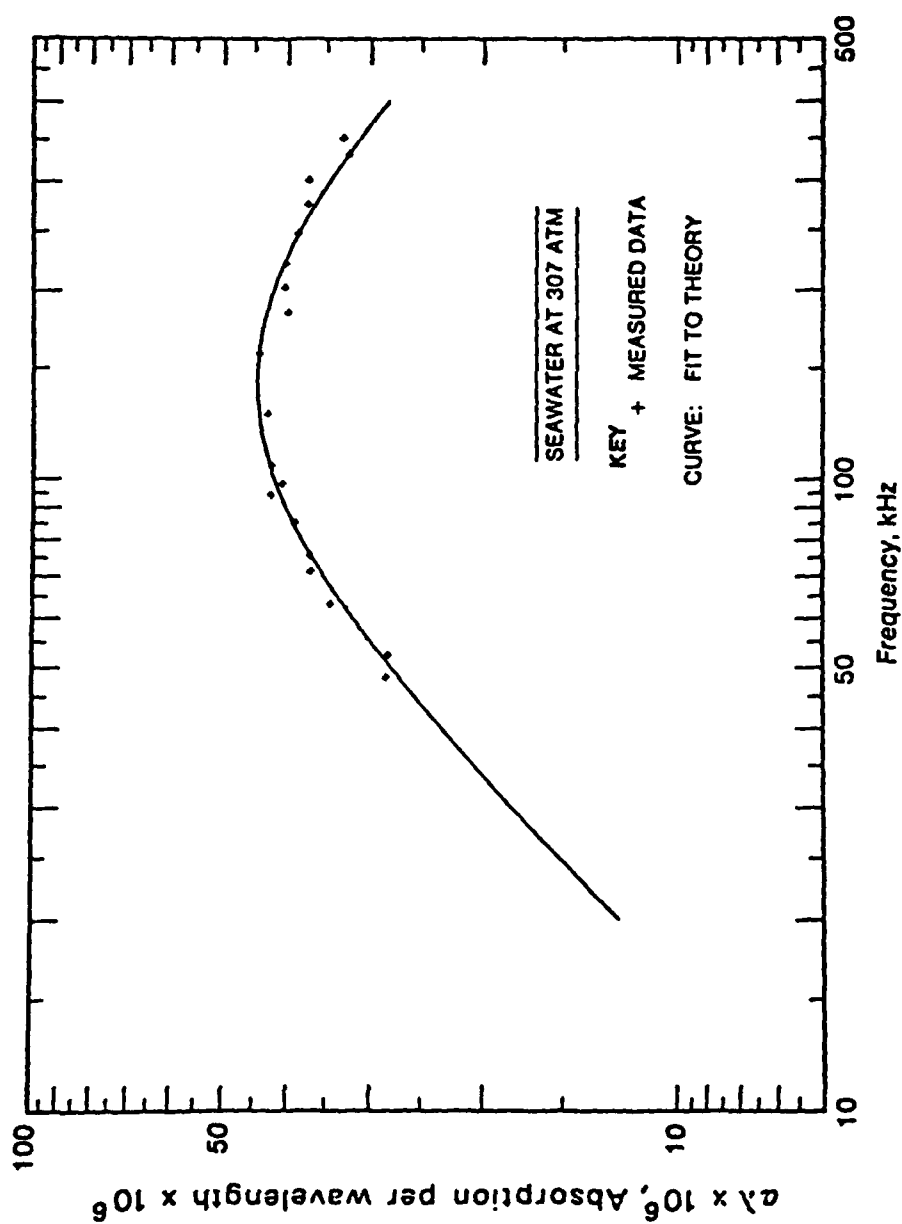
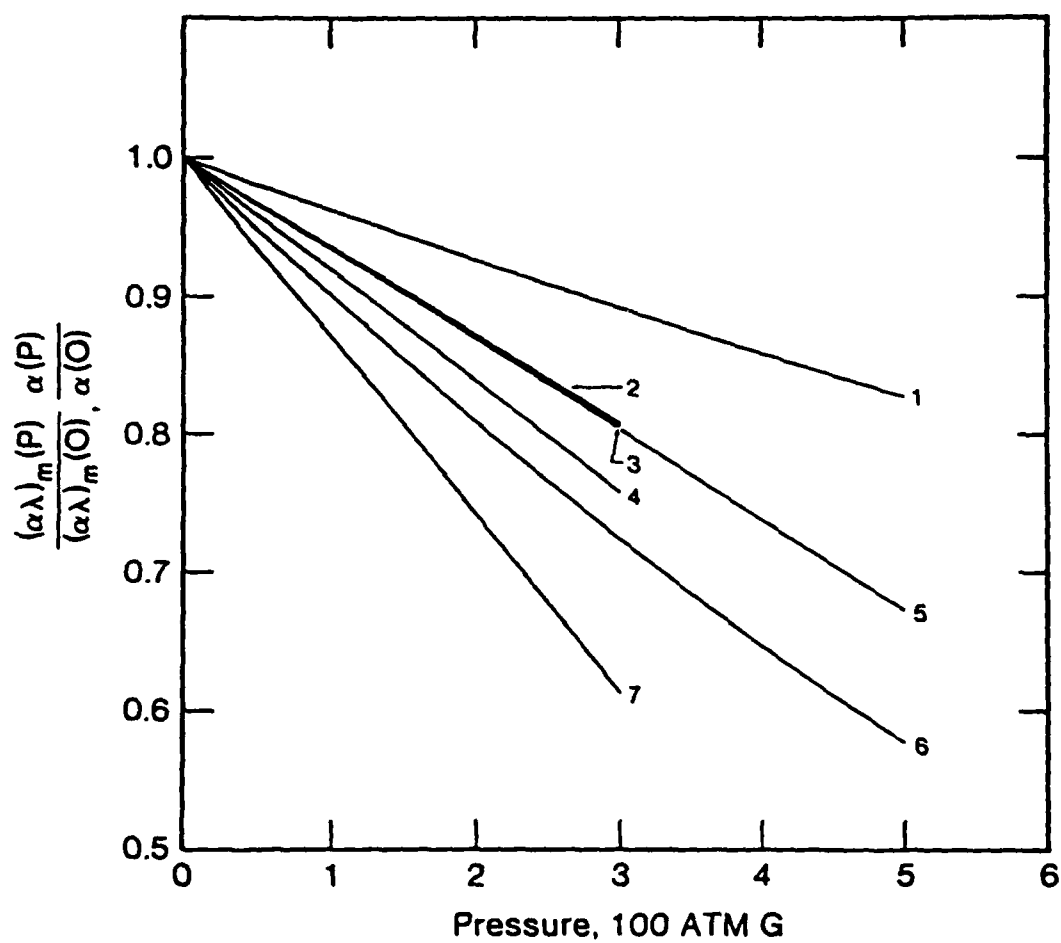
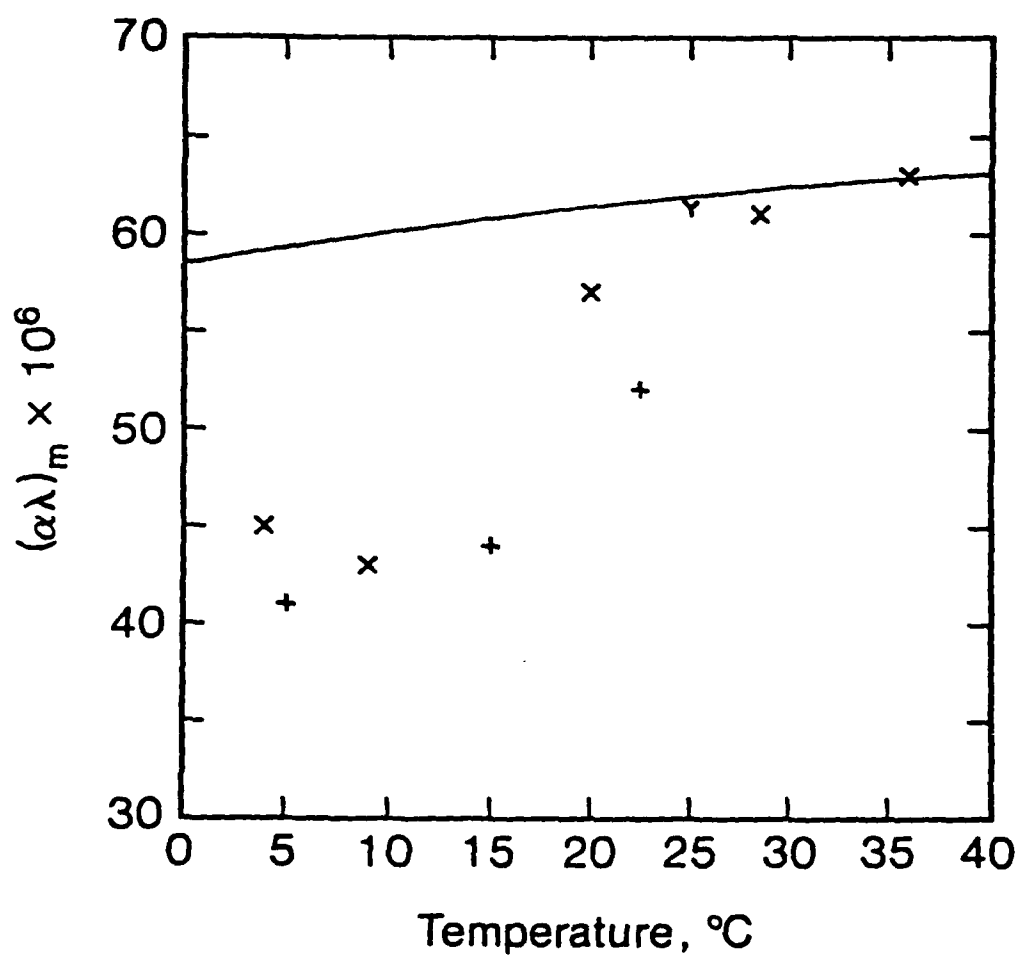


Figure V.8 Measured sound absorption data and theoretically fitted curve for Lyman and Fleming seawater at 307 atm.



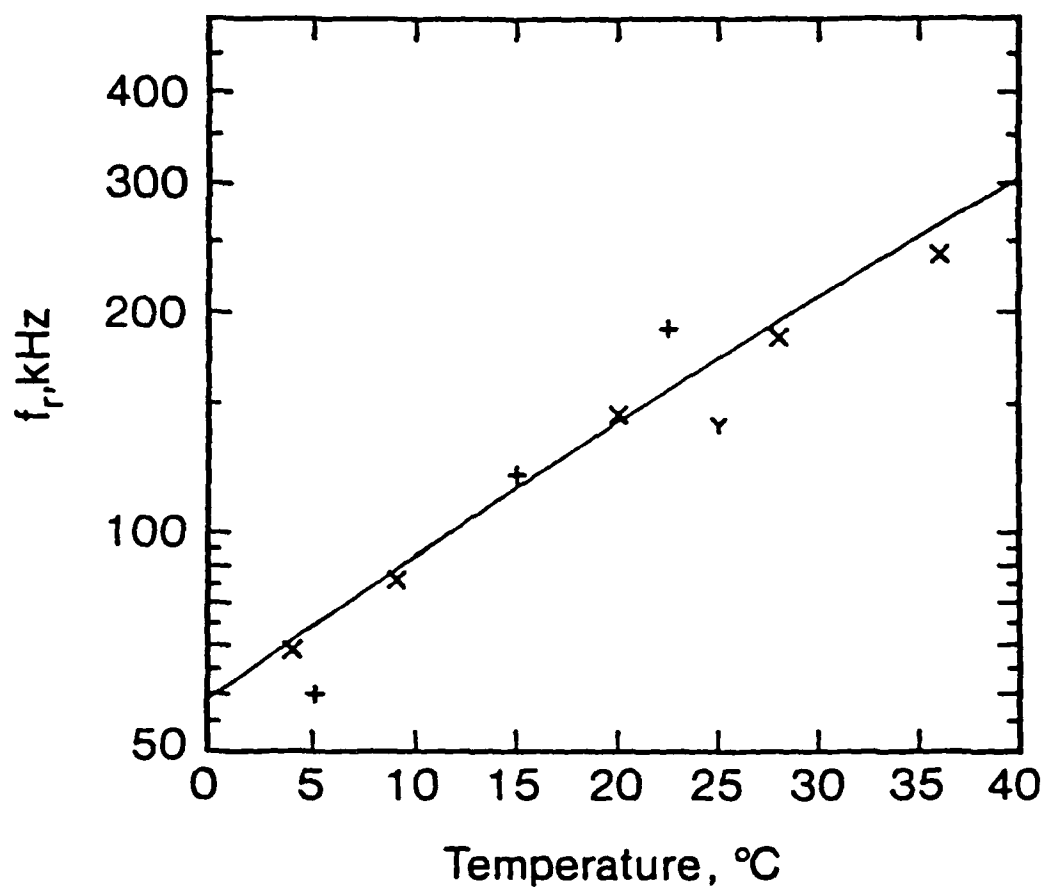
- 1 LITOVITZ AND CARNEVALE
- 2 HSU AND FISHER (.02M  $MgSO_4$ )
- 3 HSU AND FISHER (.02M  $MgSO_4$  + .6M NaCl)
- 4 HSU AND FISHER (SEAWATER)
- 5 SCHULKIN AND MARSH
- 6 FISHER
- 7 BEZDEK

Figure V.9 Pressure effect on the magnitude of sound absorption for water, magnesium sulfate solutions and seawater.

**KEY**

LINE SCHULKIN & MARSH  
+ WILSON & LEONARD  
X SIMMONS  
Y HSU & FISHER

Figure V.10 Temperature effect on the magnitude of the sound absorption in seawater.

**KEY**

LINE SCHULKIN & MARSH  
+ WILSON & LEONARD  
X SIMMONS  
Y HSU & FISHER

**Figure V.11** Temperature effect on the relaxation frequency of sound absorption in seawater.

## VI. DIFFERENTIAL EXCESS SOUND ABSORPTION AND DIFFERENTIAL MAGNESIUM SULFATE ION-PAIR CONCENTRATION IN MAGNESIUM SULFATE SOLUTION DUE TO THE ADDITION OF SODIUM CHLORIDE

### A. Introduction

In Chapter IV, the reduction in excess sound absorption due to the addition of sodium chloride was studied for .02M magnesium sulfate solution. Excess sound absorption was measured for this solution with the addition of sodium chloride at concentrations from .02 to .12M. The differential sound absorption data measured showed support for the ion association model provided for the theoretical estimation of the differential magnesium sulfate ion-pair concentration. For cases involving the addition of sodium chloride beyond concentrations of .12M, however, this model appears less capable of producing a valid prediction.

To look into this question, excess sound absorption in the mixture of .02M magnesium sulfate and .6M sodium chloride was measured using the same titanium spherical resonator technique described in Chapters II and IV. A summary of all the measured excess sound absorption data and the predicted magnesium sulfate ion-pair concentration for .02M magnesium sulfate solution is given in Table VI.1. It shows that the predicted differential magnesium sulfate ion-pair concentration is higher than the measured differential sound absorption by a factor of 2.2. A plot of these results is given in Fig. VI.1. The measured differential sound absorption data does show disagreement with the predicted differential magnesium sulfate ion-pair concentration, with the predicted  $F$ -number being greater than that actually measured.

In the study of the ion association model, the sodium chloride was assumed to be completely dissociated. However, if this assumption is not true, there would be less sodium and chloride ions available in the mixture. Consequently, there would be more magnesium sulfate ion-pairs in the mixture and thus the  $F$ -number would be smaller. An examination with respect to sodium chloride association is given in this chapter.

The disagreement between the acoustic data and the predicted result could be due to the failure of the ion association model for mixtures of high sodium chloride content. Other models might be able to offer better predictions. These possibilities are also examined in this chapter.

It is assumed that the excess sound absorption is approximately proportional to the magnesium sulfate ion-pair concentration. Thus, it is also possible that the disagreement between the acoustic data and the predicted result may be due to the invalidity of this assumption for the case of an addition of .6M sodium chloride. An examination of this aspect is given also in this chapter.

#### B. Effect of Sodium Chloride Association

Sodium chloride association has been examined in many studies.<sup>37-46,101</sup> The reported dissociation constants range from .943 to 40. For the present examination, a dissociation constant of 1. was used to estimate of the magnesium sulfate ion-pair concentration. This estimation was made by using the same ion association model provided in Chapter IV, except now the equilibrium of sodium chloride was included. The results of this estimation are shown in Table VI.1 also. It shows that for the addition of .6M sodium chloride and for a dissociation constant of 1. for sodium chloride, the differential magnesium sulfate ion-pair concentration is 22% less than that obtained when sodium chloride ion pairing is not considered. The new value of the differential magnesium sulfate ion-pair concentration is still higher than the acoustic data by a factor of 1.7. Figure VI.2 shows the decrease in the differential magnesium sulfate ion-pair concentration caused by the sodium chloride ion-pairing.

#### C. Examination of Theoretical Estimation

Stoichiometric mean activity coefficients of magnesium sulfate in the mixture of magnesium sulfate and sodium chloride have been experimentally studied by Platford<sup>54</sup> and Wu, Rush and Scatchard.<sup>56</sup> Using the results from the latter study Pitzer<sup>51-53</sup> developed the fitting

coefficients for the activity coefficient equation. The experimentally obtained results are restricted to single total ionic strength and thus are not adequate for use in this research. Robinson and Bates<sup>57</sup> have reported a hydration approach for calculating the single-ion activity coefficient in mixtures. Their method, however, depends on the stoichiometric mean activity coefficients calculated by Pitzer's equation and on the assumption that chloride ions are not hydrated. Johnson and Pytkowicz<sup>44-46</sup> have reported equations for calculating the stoichiometric association constants of  $MgSO_4^0$ ,  $NaSO_4^-$ ,  $MgCl^+$ , and  $NaCl^0$  for seawater. The equation for  $MgSO_4^0$  is valid only for ionic strength of .51 to .54. Fisher, Gieskes and Hsu<sup>101</sup> argued that the thermodynamic association constant of magnesium sulfate derived from using JP's equation, 212, is 32% greater than the value of 160 reported by Kester and Pytkowicz<sup>125</sup> and by Fisher and Fox.<sup>17</sup>

Two alternatives for estimating the magnesium sulfate ion-pair concentration are examined. One is to use the previously mentioned ion association model for the pure solution and JP's association constant equations for the mixture. According to JP, for a mixture of effective ionic strength of .51 to .54 the stoichiometric association constant is expressed by

$$K^* = e^{a_1 + a_2 I} \quad (VI.1)$$

where  $a_1 = 3.73, -0.537, 2.28$  and  $0.651$ , and  $a_2 = 0., -1.002, 0.,$  and  $-0.011$ , for  $MgSO_4^0$ ,  $NaCl^0$ ,  $NaSO_4^-$  and  $MgCl^+$ , respectively. Also,

$$K^* = \frac{[MN]}{[M][N]} \quad (VI.2)$$

where  $MN$  represents the ion-pairs,  $M$  represents the positive ions and  $N$  represents the negative ions.

Using an iterative calculation process the magnesium sulfate ion-pair concentration is then found to be  $13.16 \times 10^{-4} M$  for  $[NaCl]/[MgSO_4] = 29$ , where  $I = 0.524$ . The magnesium sulfate ion-pair concentration obtained in the previous chapter for .02M magnesium sulfate solution was  $77.78 \times 10^{-4} M$ . Thus, the differential magnesium sulfate ion-pair concentration is

calculated to be  $\Delta[MgSO_4^*]/[MgSO_4^*] = 4.910$ .

The other method of estimation is to use Pitzer's activity coefficient equation for both pure solution and mixture assuming the activity coefficient of the magnesium sulfate ion-pair is constant. The thermodynamic dissociation constant of magnesium sulfate may be expressed by

$$K = \frac{[Mg^{++}]_T [SO_4^{--}]_T \gamma_{\pm}^2}{[MgSO_4^*] f_1} \quad (VI.3)$$

for both the pure solution and the mixture. The  $[Mg^{++}]_T$  is the total concentration of the magnesium ion and so is the  $[SO_4^{--}]_T$  the total concentration of the sodium ion. The  $\gamma_{\pm}$  is the stoichiometric mean activity coefficient of  $MgSO_4$  and the  $f_1$  is the activity coefficient of the  $MgSO_4^*$  ion-pairs. Then,

$$\frac{\Delta[MgSO_4^*]}{[MgSO_4^*]} = \frac{(\gamma_{\pm}^2/f_1)_o - (\gamma_{\pm}^2/f_1)}{(\gamma_{\pm}^2/f_1)} \quad (VI.4)$$

where the subscript of  $o$  denotes the value associated with the initial pure solution.

When the activity coefficient of the magnesium sulfate ion-pair is unity, Eq. (VI.4) can then be simplified to

$$\frac{\Delta[MgSO_4^*]}{[MgSO_4^*]} = \frac{(\gamma_{\pm})_o^2 - (\gamma_{\pm})^2}{(\gamma_{\pm})^2} \quad (VI.5)$$

Using Pitzer's activity coefficient equation the results obtained are :  $(\gamma_{\pm})_o = 0.325$  for .02M magnesium sulfate solution, and  $\gamma_{\pm} = 0.306, 0.292, 0.271, 0.255, 0.233, 0.200, 0.182$  for mixtures of  $[NaCl]/[MgSO_4] = 1, 2, 4, 6, 10, 20, \text{ and } 30$ , respectively.

The results obtained by the use of these two methods are given in Table VI.2 and are plotted in Fig. VI.1. From Fig. VI.1 it can be seen that the results obtained by using JP's equation and the previous ion association model (with  $NaCl^o$  considered ) are in agreement. However, as was pointed out before, the association constant derived from JP's equation is 32% higher than that was used in previously mentioned ion association model. Also, a thermodynamic dissociation constant of 1.543 can be derived from JP's equation for  $NaCl^o$ . The disso-



ciation constant of sodium chloride used in the ion association model is 1. None of the three methods can at the present time quantitatively explain the acoustic data.

#### D. Examination of Sound Absorption Theory

This examination has to do with a further review of the variations of the physical properties of the solution and of the multistate sound absorption theory.

The influences on the viscosity, the static compressibility, and the sound speed due to the addition of sodium chloride have been discussed in Chapter IV. When their effects are examined individually, these influences are still not significant for an addition of .6M sodium chloride. Their combined effect was not investigated in this research.

Adams, Davis and Chatterjee<sup>130</sup> have commented on the partial volume dependence on concentration for magnesium sulfate solution. Yet there is no evidence of such dependence with magnesium sulfate solutions. How the addition of sodium chloride would affect the partial volume of the magnesium sulfate species in the solution is not clear.

#### E. Summary

Since none of the above methods for estimating the magnesium sulfate ion-pair concentration can quantitatively explain the acoustic results, sodium chloride ion-pairing was not successfully examined in this research. Only after a reliable method for theoretical estimation is obtained, can the acoustic data be used to argue the for sodium chloride ion-pairing.

Kurtze and Tamm<sup>3</sup> have observed that the absorption cross-section (defined as  $Q=2\alpha/nL$ , where  $n$  is the concentration of the solution in moles per unit volume and the  $L$  is the number of molecules per mole) data measured for magnesium sulfate solutions are independent of the magnesium sulfate concentration for solutions of .002M to .09M. For solutions greater than .09M, the absorption cross-section data decrease gradually as the magnesium sulfate concentration increases. This observation suggests that for pure magnesium sulfate solution the increased ionic strength would give rise to greater dissociation of magnesium sul-

fate. An attempt to correlate the greater dissociation with variations of the activity coefficient failed.

For magnesium sulfate and sodium chloride mixture, the increased ionic strength due to the addition of sodium chloride also results in reduced magnesium sulfate ion-pair concentration, although it may not be to the same extent as the effect due to the high concentration of magnesium sulfate in pure magnesium sulfate solutions. This difference, which is not understood at the present time, may be essential in explaining the difference between the measured sound absorption data and the predicted results for the magnesium sulfate and sodium chloride mixture.

Comparing the acoustic data and the results obtained from using Pitzer's equation and examining Eq. (VI.4), variations of the activity coefficient of magnesium sulfate ion-pairs with the additions of sodium chloride are noticeable. This observation can not be explained at the present time. JP<sup>47</sup> have observed that the activity coefficients of sodium chloride, hydrochloric acid and potassium chloride ion-pairs increase with increased ionic strength.

Pitzer's approach was based on the consideration of the stoichiometric osmotic coefficients without considering the ion pairing. The ion association approach studies electrolytes by assuming the existence of ion association. Statistically, when a solution becomes concentrated it is highly possible for ions to be in contact somehow. It is at this point where the present ion association theory fails to provide illumination. The different approaches would join together eventually.

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DIFFERENTIAL SOUND ABSORPTION TECHNIQUE AND EFFECT OF ION-PAIRI--ETC(U)

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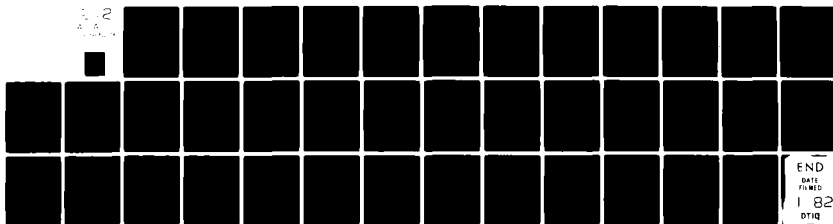
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Table VI.1  
Summary of measured sound absorption data and predicted  $MgSO_4^0$   
ion-pair concentration for solutions of  $[MgSO_4] = .02M$

$\frac{[NaCl]}{[MgSO_4]}$	0	1	2	4	6	30
$(\alpha\lambda)_m \times 10^6$	$80.75 \pm 0.55$	$71.55 \pm 1.14$	$61.50 \pm 1.13$	$52.85 \pm 0.58$	$45.35 \pm 0.53$	$20.20 \pm 0.32$
$F$	0	.129	.157	.132	.130	.100
$\frac{\Delta(\alpha\lambda)_m}{(\alpha\lambda)_m}$	0	$.129 \pm .026$	$.313 \pm .034$	$.528 \pm .028$	$.781 \pm .033$	$3.00 \pm .09$
Predicted $[MgSO_4^0] \times 10^4 M$	77.78	68.62	61.36	50.27	42.10	10.31
Predicted $F$	0	.134	.134	.137	.141	.218
Predicted $\frac{\Delta[MgSO_4^0]}{[MgSO_4^0]}$	0	.134	.268	.547	.848	6.543
Predicted* $[MgSO_4^0] \times 10^4 M$	77.78	68.71	61.63	50.98	43.24	12.80
Predicted* $F$	0	.132	.131	.131	.133	.169
Predicted* $\frac{\Delta[MgSO_4^0]}{[MgSO_4^0]}$	0	.132	.262	.526	.799	5.078

\* : considering the sodium chloride ion pairing.

**Table VI.2**  
**Differential sound absorption measured and**  
**differential magnesium sulfate ion-pair concentration**  
**predicted by different methods of estimation**

$\frac{[NaCl]}{[MgSO_4]}$	Measured $\frac{\Delta(\alpha\lambda)_m}{(\alpha\lambda)_m}$	Predicted $\frac{\Delta[MgSO_4]}{[MgSO_4]}$			
		A	B	Pitzer	JP
1	$0.129 \pm 0.026$	0.134	0.132	0.124	
2	$0.313 \pm 0.034$	0.268	0.262	0.235	
4	$0.528 \pm 0.028$	0.547	0.526	0.436	
6	$0.781 \pm 0.030$	0.848	0.799	0.618	
10		1.522	1.384	0.945	
20		3.679	3.077	1.628	
29					4.910
30	$3.000 \pm 0.090$	6.543	5.078	2.177	

A : by ion association model of this research,  $NaCl^\circ$  not considered.

B : by ion association model of this research,  $NaCl^\circ$  considered.

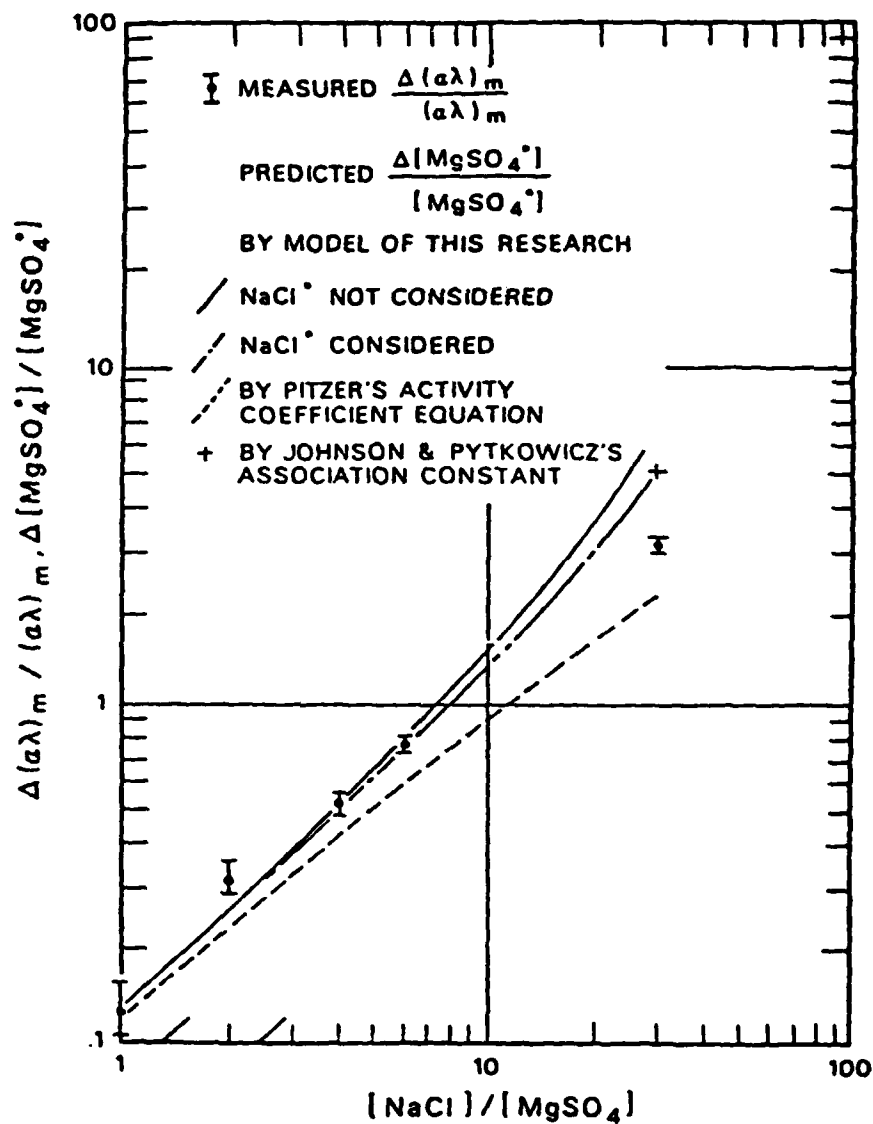


Figure VI.1 Measured differential sound absorption and predicted differential magnesium sulfate ion-pair concentration from various method of estimation.

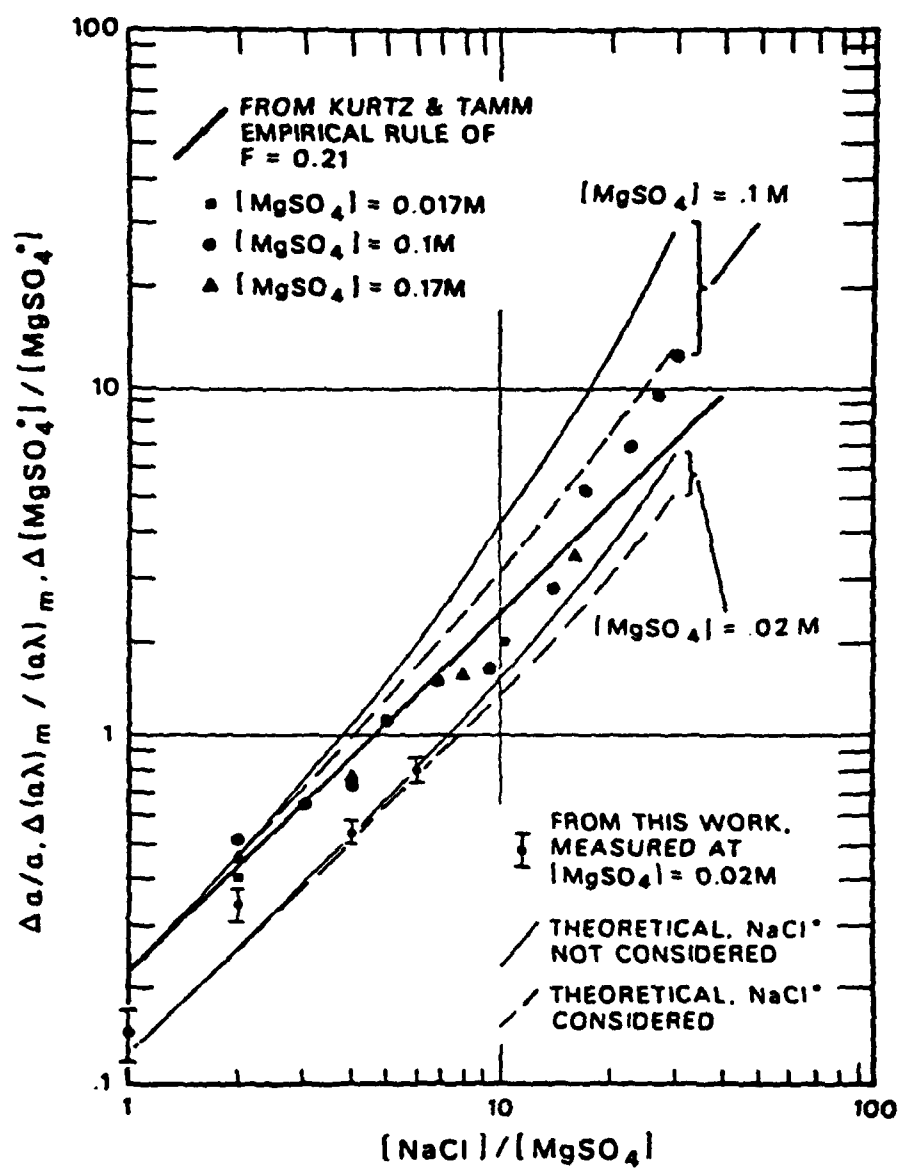


Figure VI.2 Effect of sodium chloride ion-pairing on predicted differential magnesium sulfate ion-pair concentration.



## VII. MAGNESIUM SULFATE INTERACTION IN SEAWATER FROM SOUND

### ABSORPTION MEASUREMENT AT 25 °C and 1 atm

#### A. Introduction

Kurtze and Tamm<sup>3</sup> reported that earlier investigations of seawater yielded a sound absorption which is equal to that of a .014 M magnesium sulfate solution. Using this acoustic result and considering the effective concentration of magnesium sulfate ion-pairs in magnesium sulfate solutions, Fisher<sup>107</sup> determined that in seawater 9.2 percent of magnesium ions are paired to sulfate ions and 17.5 percent of sulfate ions are paired to magnesium ions. This result agrees with other results determined chemically<sup>47,122-128</sup>, which range from 3 to 11 percent for magnesium ions and from 17.3 to 21.5 percent for sulfate ions.

Excess sound absorption has been measured for .02 M magnesium sulfate solution<sup>103</sup> and for Lyman and Fleming seawater.<sup>99</sup> The maximum absorption per wavelength in .02M magnesium sulfate solution is  $80.75 \times 10^{-6}$  and that in seawater is  $61.30 \times 10^{-6}$ . In seawater, for the frequency region of the primary relaxation of magnesium sulfate, only magnesium sulfate plays a dominant role in sound absorption.<sup>2,3,8,76,80</sup> For the same frequency region, other seawater salts exhibit no significant sound absorption. Hence, in either the pure magnesium sulfate solutions or seawater the excess sound absorption may be accounted for by the sound absorption associated with magnesium sulfate only.

The sound absorption of the primary relaxation of magnesium sulfate in aqueous solutions can be explained by the theory Eigen and Tamm<sup>10</sup> derived on the basis of a multistate association model. From this theory it was found that the excess sound absorption may be assumed to be proportional to the magnesium sulfate ion-pair concentration for magnesium sulfate solutions. Further to assume that this assumption is still valid for seawater, one can then determine the magnesium sulfate ion-pair concentration in seawater from using the measured sound absorption data for both seawater and the .02M magnesium sulfate solution, and using the estimated magnesium sulfate ion-pair concentration for .02M magnesium sulfate solution.

## B. Results

In chapter IV, for a .02M magnesium sulfate solution the ion association model approach yielded an ion-pair concentration of  $77.78 \times 10^{-4} \text{M}$ . In chapter VI, the stoichiometric mean activity coefficient obtained from Pitzer's equation<sup>46</sup> for .02M magnesium sulfate solution was 0.325. Substituting this number, .0062 for the dissociation constant and 1. for the activity coefficient of ion-pairs into Eq. (VI.3), Chap. VI, the magnesium sulfate ion-pair concentration is obtained to be  $68.15 \times 10^{-4} \text{M}$ .

In Chapter IV, the compressibility of seawater was estimated to be 6.6 percent lower than that of a .02 M magnesium sulfate solution.<sup>88</sup> Thus, according to Eq. (IV.5), Chap. IV, for a decrease in sound absorption of 24.1 percent measured in seawater comparing to the value of .02M magnesium sulfate solution, the magnesium sulfate ion-pair concentration in seawater would be :  $55.13 \times 10^{-4} \text{M}$ , based on the ion-pair concentration of  $77.78 \times 10^{-4} \text{M}$  in magnesium sulfate solution and  $48.31 \times 10^{-4} \text{M}$ , based on the other number of  $68.15 \times 10^{-4} \text{M}$ . In Lyman and Fleming seawater<sup>100</sup> the total magnesium ions concentration is .05354M and the total sulfate ions concentration is .02823 M. Hence, in seawater, the percentage of the total magnesium ions that paired to sulfate ions is 9.0-10.3 percent and that of sulfate ions is 17.1-19.5 percent. These outcomes should represent the limits of pairing between the magnesium and sulfate ions in seawater.

## VIII. CONCLUSION

The measuring technique developed was shown dependable for further applications. The pressure range of this research was limited to 307 atm due to safety consideration in regard to the titanium sphere. This range covers about half the depth of the sea. For this range an approximately linear pressure dependence of the sound absorption was obtained in this research for seawater. For deeper sea depths the pressure dependence of the sound absorption is still unknown. Thus, the possibility of a different pressure effect in this deeper region can not be ruled out, since Fisher's study for .5M magnesium sulfate solution measured at pressures up to 1333 atm found a quadratic dependence on the pressure. Nevertheless, sound absorption measurement can be further carried to higher pressure range when there is a resolution for a qualified resonator sphere.

The results of sound absorption measurements for sodium chloride and sodium sulfate solutions clarified the previously reported results related to these solutions at 1 atm. The pressure measurements of the sodium chloride solution provide new acoustic data. The excess sound absorption in these two solutions was not detected in the frequency region of 30 to 300 KHz. Hence, the excess sound absorption in magnesium sulfate-sodium chloride mixtures was proved dependent only on the magnesium sulfate equilibrium in the mixtures.

The differential sound absorption technique is shown capable of proving the existence of the unsymmetrical ion-pairs in the mixture of magnesium sulfate and sodium chloride, and of evaluating the dissociation constants pertaining to these ion-pairs. The differential sound absorption technique serves as an independent method to quantitatively study the ion-pairing in magnesium sulfate and sodium chloride mixtures. Further studies may be extended to other magnesium sulfate and alkali chloride systems. The acoustic data obtained from these systems would be useful for ion-pairing studies of other unsymmetrical alkali sulfate ion-pairs. These studies would be beneficial to the electrolyte theory and the sound absorption theory since these theories are still in need of improvement.

Only an initial study of the interpretation of the differential sound absorption in the mixture of .02M magnesium sulfate and .6M sodium chloride was given. The acoustic data should be able to check on the various electrolyte theories in many aspects, such as the activity coefficient of the ions and the ion-pairs, the dissociation constant, the distance parameter, the partial volume of the species in the solution, the structure of the ion-pairs distribution, and so on. More detailed analyses are still needed for a better understanding of sound absorption in a mixture of high sodium chloride concentration. This mixture plays an intermediate role between magnesium sulfate solution and seawater.

The extensive study of the differential sound absorption for the magnesium sulfate-sodium chloride system further enlarged the partnership between the sound absorption and the electrical conductance measurements in studying electrolytes. Previous investigations have only applied this partnership to studies of pure magnesium solutions. This research further provided sound absorption data for mixtures.

The greater pressure factor on sound absorption shown by seawater was not explained. The cause may be found by undertaking more sound absorption measurements, with additions of other salts to the magnesium sulfate and sodium chloride mixture. It has to be due to the interactions of magnesium and sulfate ions with other seawater salts.

The observation of no significant shift of the relaxation frequency with pressure for magnesium sulfate solution, for mixture of magnesium sulfate and sodium chloride, and for seawater signals the probability that no significant variation of the reaction rate could be caused by the addition of sodium chloride and other major seawater salts. Further studies in this area are still needed.

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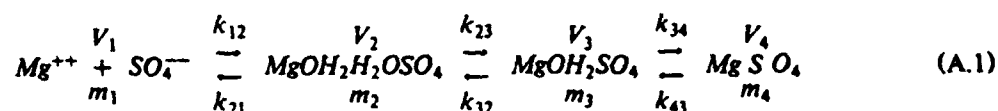
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## APPENDIX A

### Eigen and Tamm<sup>10</sup> sound absorption theory based on a four-state association model

The four-state model from which sound absorption theory was developed is



where  $V_i$  and  $m_i$  are the partial volumes and the concentrations of the species in states 1, 2, 3 and 4, respectively, and  $k_{ij}$  are the reaction rates.

The primary excess absorption relaxation in the 100 KHz region is associated with step 3 where the water molecule bonded to magnesium is repelled. The second relaxation in the 200 MHz is with step 1 and the likely third one in the 10 MHz region is with step 2.

The equilibrium constants,  $K_{ij}$ , are related to the concentrations,  $m_i$ , and the reaction rates,  $k_{ij}$ , as follows:

$$K_{12} = \frac{m_1^2 \pi^f}{m_2} = \frac{k_{21} f_{\pm}^2}{k_{12}} \quad (\text{A.2})$$

$$K_{23} = \frac{m_2}{m_3} = \frac{k_{32}}{k_{23}} \quad (\text{A.3})$$

$$K_{34} = \frac{m_3}{m_4} = \frac{k_{43}}{k_{34}} \quad (\text{A.4})$$

where  $\pi^f = f_{\pm}^2$  assuming the activity coefficient of ion-pair is unity,  $f_{\pm} = (\gamma_{\text{Mg}^{++}} \gamma_{\text{SO}_4^{--}})^{1/2}$  is the mean activity coefficient of the magnesium and sulfate ions.

For a conventional two-state association model, the equilibrium constant,  $K_m$ , is expressed by

$$K_m = \frac{ma^2 f_{\pm}^2}{1-a} \quad (\text{A.5})$$

where  $a = m_1/m$  is the degree of dissociation and  $m = m_1 + m_2 + m_3 + m_4$  is the formal concentration of the magnesium sulfate in the solution. Since the total ion-pair concentration is  $m(1-a) = m_2 + m_3 + m_4$  Eq. (A.5) can be written as

$$K_m = \frac{m_1^2 f_{\pm}^2}{m_2 + m_3 + m_4} \quad (\text{A.6})$$

Substituting Eqs. (A.2) to (A.4) into Eq. (A.6), then

$$K_m = \frac{K_{12}K_{23}K_{34}}{1 + K_{34}(1 + K_{23})} \quad (\text{A.7})$$

The relaxation frequency of the primary sound absorption is

$$\kappa_{III} = 2\pi f_r = k_{43} + \frac{k'_{23}k_{34}}{k'_{23} + k_{32}} \quad (\text{A.8})$$

where

$$k'_{23} = \frac{k'_{12}k_{23}}{k'_{12} + k_{12}} \quad (\text{A.9})$$

$$k'_{12} = k_{12} m a f_{\pm}^2 \left( 2 + \frac{\partial \ln f_{\pm}^2}{\partial \ln a} \right) \quad (\text{A.10})$$

and  $k_{12}$  is the  $k_{12}$  at zero ionic strength.

The sound absorption per wavelength associated with the relaxation frequency,  $\kappa_{III}$ , is

$$\alpha \lambda = \frac{\pi \beta_{III}}{\beta_0} \frac{\omega \kappa_{III}}{(\omega^2 + \kappa_{III}^2)} \quad (\text{A.11})$$

where  $\alpha$  is the sound absorption constant,  $\lambda$  is the wavelength of the sound wave,  $\beta_0$  is the static compressibility of the solution,  $\omega = 2\pi f$ ,  $f$  is the frequency.

$$\beta_{III} = \frac{(m'_1 + m_2 + m_3)m_4}{m'_1 + m_2 + m_3 + m_4} \frac{(\Delta V_{III})^2}{RT} \quad (\text{A.12})$$

$$m'_1 = m_1 \left( 2 + \frac{\partial \ln \pi f}{\partial \ln a} \right)^{-1} \quad (\text{A.13})$$

$$\Delta V_{III} = (V_4 - V_3) + \frac{k_{32}}{k'_{23} + k_{32}} \Delta V_{II} \quad (\text{A.14})$$

$$\Delta V_{II} = (V_3 - V_2) + \frac{k_{21}}{k'_{12} + k_{21}} (V_2 - V_1) \quad (\text{A.15})$$

$R$  is the gas constant and  $T$  is the temperature.

Listed in the following pages are dynamic parameters obtained by various investigators.

The parameters obtained by Eigen and Tamm<sup>10</sup> which best fit to the acoustic data obtained by Kurtze and Tamm<sup>3</sup> at 20 °C and atmospheric pressure for aqueous solutions of concentrations up to .2M are:

PARAMETERS	MODEL I	MODEL II
$K_{12}$	0.02M	0.04M
$K_{23}$	0.5	1.0
$K_{34}$	7.5	9.0
$\Delta V_{12} = V_1 - V_2$	0	0
$\Delta V_{23} = V_2 - V_3$	-14 cc/mole	-18 cc/mole
$\Delta V_{34} = V_3 - V_4$	-3 cc/mole	-3 cc/mole
$K_m$	0.0073M	0.019M

Model II was shown by Fisher<sup>73</sup> to explain the pressure results for magnesium sulfate solutions, however, its equilibrium constant seems too high. Fisher and Fox<sup>17</sup> reported a summary of the parameters as follows:

$K_{12}(M)$	.024	.040	.025	.020	.027
$K_{23}$	0.50	1.00	0.31	0.51	0.50
$K_{34}$	7.5	9.0	2.5	5.8	5.6
$\Delta V_{12}(\text{cc/mole})$	0	0	-14	0	-7
$\Delta V_{23}(\text{cc/mole})$	-14	-18	+13	-10	+3
$\Delta V_{34}(\text{cc/mole})$	-3	-3	-5	-3	-5
REMARKS	a	b	c	d	e

Remarks: a. Eigen and Tamm,<sup>10</sup> Model I b. Eigen and Tamm,<sup>10</sup> Model II c. Bechteler, Breitschwerdt and Tamm<sup>64</sup> d. Atkinson and Petrucci,<sup>65</sup> Millero and Masterton<sup>68</sup> e. Garland, Patel and Atkinson<sup>114</sup> (Seawater)



Atkinson and Petrucci,<sup>65</sup> Fritsch, Montrose, Hunter and Dill,<sup>62</sup> Bechtler, Breitchwerdt and Tamm<sup>64</sup> have measured sound absorption at different concentrations and temperatures.

Their results of the parameters are summarized as follows:

$k_{12} \times 10^{-10} (1/M \text{ sec})$	4.6	2.8	2.	
$k_{21} \times 10^{-8} (1/\text{sec})$	8.	5.6	4.4	10.
$K_{12} (M)$	0.017	0.020	0.023	0.025
$k_{23} \times 10^{-8} (1/\text{sec})$	10.	0.72	7.	
$k_{32} \times 10^{-8} (1/\text{sec})$	5.	0.37	2.	4.5
$K_{23}$	0.5	0.51	0.3	0.31
$k_{34} \times 10^5 (1/\text{sec})$	1.	1.4	1.4	
$k_{43} \times 10^5 (1/\text{sec})$	8.	8.	8.6	7.1
$K_{34}$	7.5	5.8	6.	2.5
$K_m$	.0051	.0061	.0047	.0045
$m$ (Mole)	$\leq 0.2$	0.09889	0.2	0.5
		0.1493		
		0.1965		
$T$ (°C)	20	25	25	20
Remarks	a	b	c	d

a: Eigen and Tamm as cited in Atkinson and Petrucci<sup>65</sup>

b: Atkinson and Petrucci<sup>65</sup>

c: Fritsch, Montrose, Hunter and Dill<sup>62</sup>

d: Bechtler, Breitchwerdt and Tamm<sup>64</sup>

## APPENDIX B

Raw data of the decay rate of sound wave

measured at 25 °C with deionized water in the titanium sphere

FREQUENCY(KHz)	DECAY RATE(dB/sec)	T(°C)*	DEVIATION(°C)
10.53115	3.87	24.915	-.075
13.272885	3.6	24.955	-.045
16.28053	3.3	24.92	-.080
20.19143	1.64	25.035	+.035
22.77192	1.0	25.0	0
25.35171	1.03	25.01	+.010
29.3278	1.13	25.015	+.015
33.0777	1.15	24.98	-.020
45.49077	1.36	25.045	+.045
60.06839	2.13	24.99	-.010
75.2511	3.4	25.005	+.005
98.3517	4.7	25.05	+.050
108.7039	6.0	25.0	0
120.2775	7.62	24.98	-.020
130.1295	10.2	24.975	-.025
140.3688	12.3	24.975	-.025
151.0835	14.85	25.03	+.030
200.6096	29.7	25.035	+.035
250.216	54.0	25.02	+.020
299.1351	74.6	25.0575	+.058

\* : Average value of the thermistor readings.

## APPENDIX C

Raw data of the decay rate of sound wave and  $\alpha/f^2$  values

for the following solutions in the titanium sphere:

deionized water, sodium sulfate and sodium chloride solutions

1. Deionized water at 1 atm.

FREQUENCY(KHZ)	DECAY RATE(dB/sec)	$\alpha/f^2 \times 10^{15}(\text{sec}^2/\text{m})$
20.19	1.64	309.43
22.77	1.0	148.34
25.35	1.03	123.27
29.33	1.13	101.06
33.08	1.15	80.85
45.49	1.36	50.55
60.07	2.13	45.41
75.25	3.4	46.19
98.35	4.7	37.38
108.70	6.0	39.06
120.28	7.62	40.52
130.13	10.2	46.33
140.37	12.3	48.02
151.08	14.85	50.04
200.61	29.7	56.77
250.22	54.0	66.35
299.14	74.6	64.13

2. .03M sodium sulfate solution at 1 atm.

FREQUENCY(KHz)	DECAY RATE(dB/sec)	$\alpha/f^2 \times 10^{15}(\text{sec}^2/\text{m})$
22.85	0.92	135.05
25.44	1.09	129.08
45.68	1.7	62.45
60.29	2.6	54.84
75.53	2.7	36.29
109.09	5.9	38.01
130.099	8.7	39.41
151.32	14.7	49.22
226.54	36.6	54.68
259.74	55.0	62.50
299.92	65.0	55.40

## 3. .16M sodium chloride solution at 1 atm.

FREQUENCY(KHz)	DECAY RATE(dB/sec)	$\alpha/f^2 \times 10^{15}(\text{sec}^2/\text{m})$
22.02	1.34	211.21
46.08	1.8	64.77
60.49	2.4	50.12
75.77	3.4	45.25
109.44	5.5	35.08
130.53	9.0	40.36
170.94	22.2	58.05
227.24	40.8	60.37
260.64	50.0	56.24
300.45	63.3	53.58

## 4. .58M sodium chloride solution at 1 atm.

FREQUENCY(KHz)	DECAY RATE(dB/sec)	$\alpha/f^2 \times 10^{15}(\text{sec}^2/\text{m})$
23.35	1.6	220.60
30.06	1.4	116.41
46.63	2.24	77.41
61.45	2.8	55.73
100.82	5.0	36.97
111.42	5.5	33.29
123.01	7.5	37.25
133.15	10.2	43.23
143.79	10.5	38.17
154.73	16.8	52.73
205.17	35.3	63.02
256.22	50.0	57.24
306.09	73.2	58.71
358.10	82.2	48.17

## 5. .58M sodium chloride solution at 71 atm.

FREQUENCY(KHz)	DECAY RATE(dB/sec)	$\alpha/f^2 \times 10^{15}(\text{sec}^2/\text{m})$
23.51	1.7	229.49
30.09	1.5	123.61
61.55	2.2	43.34
78.05	4.2	51.45
101.02	5.2	38.02
144.37	13.3	47.61
155.26	18.4	56.96
205.57	33.7	59.50
256.56	48.4	54.87
306.81	68.2	54.06
358.85	71.4	41.37

## 6. .58M sodium chloride solution at 123 atm.

FREQUENCY(KHz)	DECAY RATE(dB/sec)	$\alpha/f^2 \times 10^{15}(\text{sec}^2/\text{m})$
25.97	1.8	198.06
46.89	2.0	67.50
61.87	2.1	40.70
101.58	4.8	34.51
145.08	15.0	52.87
207.21	36.6	63.24
258.20	42.3	47.07
308.97	66.7	51.84
361.00	73.2	41.67

## 7. .58M sodium chloride solution at 185 atm.

FREQUENCY(KHz)	DECAY RATE(dB/sec)	$\alpha/f^2 \times 10^{15}(\text{sec}^2/\text{m})$
24.04	1.84	234.69
62.21	2.2	41.89
101.95	4.84	34.32
156.75	14.3	42.89
207.98	34.5	58.78
259.07	50.3	55.23
309.99	67.4	51.69
362.44	70.92	39.79

## 8. .58M sodium chloride solution at 246 atm.

FREQUENCY(KHz)	DECAY RATE(dB/sec)	$\alpha/f^2 \times 10^{15}(\text{sec}^2/\text{m})$
62.59	2.4	44.85
102.38	5.5	38.41
157.31	19.5	57.69
208.85	37.0	62.11
260.56	50.0	53.92
311.34	63.8	48.19
363.98	76.9	42.50

## 9. .58M sodium chloride solution at 307 atm.

FREQUENCY(KHz)	DECAY RATE(dB/sec)	$\alpha/f^2 \times 10^{15}(\text{sec}^2/\text{m})$
62.97	2.3	42.19
102.999	5.2	35.65
158.13	16.4	47.71
210.01	34.7	57.23
262.03	55.0	58.27
313.38	75.0	55.55
366.04	96.7	52.49

## APPENDIX D

**Data of measured decay rate, background correction and absorption  
per wavelength versus frequency, and results of maximum absorption  
per wavelength, relaxation frequency and standard deviation  
obtained by the curve fitting program**

**Data are read using the format shown below:**

Frequency(KHz)	$\alpha \lambda \times 10^6$	Decay Rate(dB/sec)	Correction(dB/sec)
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
<hr/>			
Not data but index for programming			
<hr/>			
Solution measured			
<hr/>			
2 times the maximum absorption per wavelength			
<hr/>			
Relaxation frequency(KHz)			
<hr/>			
Standard deviation of the maximum absorption per wavelength			
<hr/>			
Range of the maximum absorption per wavelength			
<hr/>			
Maximum Absorption	Relaxation Frequency	Standard Deviation	
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.
.	.	.	.

Obtained by setting the relaxation frequency first as was described in Chapter II.

**Data files are:**

```

HSUDATAA  HSUDATAB  HSUDATAC  HSUDATAD
HSUDATAE  HSUDATAF  HSUDATAG  HSUDATAH
HSUDATAW  HSUDATAX  HSUDATAY  HSUDATAZ

```

## HSUDATAA (04/16/81)

100	10.55040,10.148	4.8,3.87
200	13.29634,13.940	5.2,3.59
300	16.31151,18.280	5.88,3.29
400	20.22966,25.610	6.1,1.60
500	22.80917,19.685	5.1,1.20
600	33.13120,28.876	9.6,1.29
700	45.59286,47.220	20.3,1.6
800	59.91120,57.246	31.9,2.11
900	98.51550,72.925	67.1,4.70
1000	108.9238,76.046	78.0,6.05
1100	120.3874,79.565	90.9,7.70
1200	130.1158,81.756	102.0,9.60
1300	137.2426,79.105	105.3,11.00
1400	139.8165,80.284	109.0,11.50
1500	151.3296,78.360	117.6,14.60
1600	170.0862,87.013	149.0,20.45
1700	209.6470,79.352	178.6,34.10
1800	226.5585,73.861	185.2,39.85
1900	259.7118,69.641	208.3,51.20
2000	274.2761,64.516	210.0,56.30
2100	279.7469,65.600	217.4,58.00
2200	289.5926,65.823	227.3,61.50
2300	299.9860,62.287	227.3,65.00
2400	<hr/> 0.0C <hr/>	
2500	0.02M MGSD4 AT 1 ATM <hr/>	
2600	2X(MAX ABSORPTION)X1M=161.5 <hr/>	
2700	RELAXATION FREQUENCY=148.9 KHZ <hr/>	
2800	(SIGMA)X1M=.55336136 <hr/>	
2900	MAX ADESCPTION RANGE <hr/>	
3000	80.20 < 80.75 < 81.30 <hr/>	
3100	MAX AB	REL FR SIGMA
3200	81.7	125KHZ 1.136
3300	81.4	130 .945
3400	81.2	135 .781
3500	81.0	140 .653
3600	80.83	145 .573
3700	80.75	148.9 .553
3800	80.7	150 .555
3900	80.6	155 .595
4000	80.6	160 .678
4100	80.5	165 .786
4200	80.5	170 .907
4300	80.5	175 1.033
4400	80.6	180 1.160

## HSUDATAB (04/16/81)

100	23.5510,21.705	5.62,1.18
200	30.8866,27.769	8.7,1.25
300	32.8147,28.138	9.3,1.28
400	34.1998,30.701	10.44,1.32
500	39.8421,34.242	13.3,1.45
600	41.3039,33.866	13.64,1.49
700	45.8372,34.937	15.52,1.61
800	61.8767,49.473	28.8,2.21
900	79.1000,53.256	39.85,3.26
1000	89.0147,56.921	47.96,3.95
1100	101.6023,63.024	60.6,4.98
1200	124.0949,63.309	76.6,8.36
1300	135.0359,62.579	83.9,10.50
1400	145.4247,63.452	93.0,12.85
1500	155.5350,64.823	103.9,16.10
1600	187.4702,60.644	125.0,26.25
1700	215.5431,58.965	147.1,36.50
1800	250.0860,60.122	178.6,46.00
1900	270.4073,58.627	193.2,55.50
2000	299.6777,50.711	197.0,65.00
2100	349.5246,43.692	212.8,60.00
2200	0.0	
2300	.02 M MSGG4 AT 307.1 ATM	
2400	2X(MAX ABSORPTION)X1M =129.9	
2500	RELAXATION FREQUENCY =145.1 KHZ	
2600	(SIGMA)X1M=.42597376	
2700	MAX ABSORPTION RANGE	
2800	64.524 < 64.95 < 65.376	
2900	MAX AB	REL FR SIGMA
3000	64.2	120 KHZ 1.103
3100	64.4	125 .903
3200	64.5	130 .723
3300	64.7	135 .572
3400	64.8	140 .466
3500	64.95	145.1 .426
3600	65.1	150 .459
3700	65.2	155 .545
3800	65.4	160 .658
3900	65.5	165 .783
4000	65.7	170 .911
4100	65.9	175 1.039



## HSUDATAC (04/15/81)

100	22.82969,16.541,	4.48,1.2
200	33.17980,28.098,	9.38,1.285
300	45.60340,35.293,	15.58,1.6
400	59.96139,45.086,	27.68,2.115
500	75.65120,68.589,	48.08,3.01
600	98.63910,65.653,	60.98,4.73
700	109.0214,62.188,	64.94,6.05
800	120.5611,67.160,	79.13,7.80
900	130.1825,69.758,	88.45,9.61
1000	137.3510,66.293,	90.09,11.0
1100	139.8569,79.049,	107.53,11.5
1200	142.4222,72.590,	102.00,12.2
1300	151.4249,73.004,	110.62,14.6
1400	170.3037,77.498,	135.14,20.5
1500	182.6252,79.996,	151.5,24.6
1600	209.6701,67.044,	156.3,34.2
1700	226.6848,67.192,	172.4,40.1
1800	259.8042,60.798,	188.7,51.5
1900	274.4704,55.536,	168.7,56.3
2000	279.8936,50.889,	181.82,58.1
2100	290.1333,51.284,	190.84,61.6
2200	0.00	
2300	0.02M H2SO4 + 0.02M NaCl	
2400	2X(MAX ABSORPTION)XIM=143.1	
2500	RELAXATION FREQUENCY=145.4 KHZ	
2600	(SIGMA)XIM=1.14402746	
2700	MAX ABSORPTION RANGE	
2800	70.41 < 71.55 < 72.69	
2900	MAX AE REL FR SIGMA	
3000	72.9 110KHZ 1.931	
3100	72.6 115 1.733	
3200	72.3 120 1.561	
3300	72.0 125 1.415	
3400	71.8 130 1.299	
3500	71.7 135 1.214	
3600	71.6 140 1.162	
3700	71.55 145.4 1.144	
3800	71.5 150 1.156	
3900	71.5 155 1.195	
4000	71.5 160 1.254	
4100	71.5 165 1.329	
4200	71.6 170 1.415	
4300	71.7 175 1.508	
4400	71.8 180 1.606	
4500	72.0 185 1.707	
4600	72.2 190 1.809	
4700	72.3 195 1.910	
4800	72.6 200 2.011	
4900	75.5 250 2.914	

HSUDATAD (04/16/81)

100	22.84993,15.115	4.2,1.2
200	33.19115,26.042	8.8,1.292
300	45.64070,35.062	15.5,1.6
400	59.99720,43.914	25.0,2.115
500	75.71790,60.187	42.6,3.016
600	98.71870,52.795	50.0,4.73
700	109.0675,57.581	60.6,6.05
800	120.7308,57.883	68.5,7.8
900	130.2305,58.505	75.8,9.62
1000	137.4025,57.309	79.4,11.0
1100	139.8802,65.268	90.9,11.6
1200	142.4811,55.269	80.6,12.2
1300	151.4813,68.097	104.2,14.6
1400	170.4190,64.718	116.3,20.5
1500	182.6151,66.385	129.9,24.6
1600	209.7043,65.606	153.8,34.3
1700	226.2365,60.194	158.7,40.1
1800	259.8808,47.490	158.7,51.5
1900	274.5665,47.424	169.5,56.4
2000	290.2954,43.863	172.4,61.8
2100	300.0085,37.761	163.4,65.0
2200	0.00	
2300	0.02M HGS04 + 0.04M NaCl	
2400	2X(MAX ABSORPTION)X1M=123.0	
2500	RELAXATION FREQUENCY=140.3 KHZ	
2600	(SIGMA)X1M=1.13004013	
2700	MAX ABSORPTION RANGE	
2800	60.37 < 61.50 < 62.63	
2900	MAX AE	REL FR SIGMA
3000	62.2	110KHZ 1.617
3100	62.4	115 1.471
3200	62.2	120 1.349
3300	61.9	125 1.254
3400	61.7	130 1.185
3500	61.6	135 1.144
3600	61.5	140.3 1.130
3700	61.4	145 1.140
3800	61.4	150 1.172
3900	61.3	155 1.220
4000	61.4	160 1.282
4100	61.4	165 1.353
4200	61.4	170 1.431
4300	61.5	175 1.513
4400	61.6	180 1.598
4500	61.7	185 1.684
4600	61.5	190 1.771
4700	62.0	195 1.858
4800	62.2	200 1.944
4900	64.5	250 2.715

## HSUDATAE (04/16/81)

100	22.8502,12.825	3.75,1.2
200	45.7283,29.431	13.3,1.61
300	60.0805,36.757	21.3,2.118
400	75.6545,43.481	31.6,3.012
500	98.7306,47.191	45.2,4.73
600	99.0837,53.135	50.5,4.77
700	109.2623,52.210	55.6,6.05
800	120.5248,52.516	63.0,7.84
900	130.2773,53.712	70.4,9.62
1000	140.0363,55.707	79.4,11.64
1100	142.6206,55.215	80.6,12.2
1200	151.5233,54.972	87.0,14.65
1300	170.5093,49.749	94.3,20.62
1400	182.5982,48.052	101.0,24.62
1500	210.0247,50.431	126.3,34.3
1600	226.8295,46.466	131.6,40.05
1700	260.0564,45.289	153.8,51.5
1800	274.8021,42.858	158.7,56.4
1900	290.6051,34.585	149.3,62.0
2000	290.6670,46.183	178.6,62.0
2100	299.5726,39.031	166.7,65.0
2200	0.,0.	
2300	0.02M HGSO4 + 0.08M NaCl	
2400	2X(MAX ABSORPTION)X1M=105.7	
2500	RELAXATION FREQUENCY=140.9 KHZ	
2600	(SIGMA)X1M=.58211769	
2700	MAX ABSORPTION RANGE	
2800	52.27 < 52.85 < 53.43	
2900	MAX AB	REL FR SIGMA
3000	53.9	115KHZ 1.022
3100	53.6	120 .863
3200	53.4	125 .764
3300	53.2	130 .670
3400	53.0	135 .608
3500	52.85	140.9 .582
3600	52.8	145 .594
3700	52.7	150 .637
3800	52.7	155 .701
3900	52.6	160 .780
4000	52.6	165 .868
4100	52.7	170 .960
4200	52.7	175 1.053
4300	52.7	180 1.147
4400	52.8	185 1.241
4500	52.9	190 1.332
4600	53.0	195 1.422
4700	53.1	200 1.510
4800	54.7	250 1.259

## HSUDATAF (04/16/81)

100	22.92578,11.751	3.54,1.2
200	45.82620,22.322	10.5,1.615
300	60.17070,29.041	17.3,2.122
400	75.75480,38.875	28.6,3.02
500	98.99870,40.981	40.0,4.76
600	109.3299,46.797	50.5,6.06
700	120.9718,46.024	56.2,7.84
800	130.2566,45.678	61.3,9.62
900	140.2417,46.210	68.0,11.71
1000	142.5061,47.019	70.4,12.2
1100	151.6578,48.167	78.1,14.65
1200	170.7331,42.010	83.0,20.7
1300	183.2356,40.714	89.5,24.7
1400	210.1674,40.756	108.7,34.3
1500	227.1254,42.224	123.5,40.2
1600	260.2806,41.799	146.0,51.5
1700	290.6010,34.942	150.2,62.0
1800	300.2401,34.894	156.2,65.2
1900	0.0	
2000	0.02M MGS04 + 0.12M NaCl	
2100	2X(MAX ABSORPTION)X1M=90.7	
2200	RELAXATION FREQUENCY=147.6 KHZ	
2300	(SIGMA)X1M=.53088345	
2400	MAX ABSORPTION RANGE	
2500	44.82 < 45.35 < 45.88	
2600	MAX AB REL FR SIGMA	
2700	46.0 115KHZ 1.072	
2800	45.8 120 .936	
2900	45.7 125 .814	
3000	45.5 130 .709	
3100	45.5 135 .625	
3200	45.4 140 .565	
3300	45.4, 145 .535	
3400	45.35 147.6 .531	
3500	45.4 150 .534	
3600	45.4 155 .560	
3700	45.4 160 .606	
3800	45.5 165 .666	
3900	45.5 170 .734	
4000	45.6 175 .808	
4100	45.7 180 .884	
4200	45.8 185 .960	
4300	45.9 190 1.037	
4400	46.1 195 1.113	

## MSUDATAG (04/16/81)

100	34.5101,9.921	4.3,1.326
200	37.8335,10.042	4.7,1.4
300	45.7871,12.396	6.54,1.61
400	59.7666,13.060	8.89,2.1
500	61.5939,12.729	9.01,2.2
600	75.6869,13.827	12.1,3.01
700	79.9251,16.205	14.55,3.3
800	97.1560,18.142	19.87,4.56
900	99.9279,17.835	20.34,4.86
1000	123.7053,19.330	28.99,8.22
1100	155.3349,20.871	43.96,15.8
1200	174.2182,16.364	49.39,21.6
1300	205.5521,16.820	62.99,32.9
1400	224.9352,18.830	76.19,39.4
1500	257.7388,20.177	95.92,50.75
1600	274.7454,19.426	102.56,56.2
1700	308.1091,17.229	113.31,67.2
1800	0.0	
1900	.02 M HGSO4 + .6 M NaCl AT 1 ATM	
2000	2X(MAX ABSORPTION)XIM=40.4	
2100	RELAXATION FREQUENCY=162.3 KHZ	
2200	(SIGMA)XIM=.32112390	
2300	MAX ABERSCRIPTION RANGE	
2400	19.88 < 20.20 < 20.52	
2500	MAX AB	REL FR SIGMA
2600	19.8	130KHZ -518
2700	19.8	135 -466
2800	19.9	140 -419
2900	20.0	145 -381
3000	20.0	150 -352
3100	20.1	155 -332
3200	20.2	160 -322
3300	20.2	162.3 -321
3400	20.3	165 -323
3500	20.3	170 -331
3600	20.4	175 -347
3700	20.5	180 -368
3800	20.6	185 -393
3900	20.6	190 -420
4000	20.7	195 -449
4100	20.8	200 -479

## HSUDATAH (04/17/81)

100	35.0238,7.067	3.49,1.34
200	46.9598,9.010	5.32,1.645
300	62.0739,11.685	8.51,2.21
400	63.1004,11.586	8.64,2.29
500	77.7611,12.866	11.85,3.16
600	80.0418,13.600	12.77,3.315
700	112.3158,14.894	20.98,6.45
800	124.0056,14.985	24.49,8.35
900	155.5261,17.661	40.0,16.08
1000	174.9151,16.856	47.51,21.9
1100	207.0142,15.967	62.31,33.6
1200	258.7295,14.622	83.86,51.0
1300	275.7948,11.659	84.93,57.0
1400	300.0127,11.604	95.24,65.0
1500	309.2271,14.077	108.11,70.3
1600	0.00	
1700	.02M HGS04 + .6M NaCl AT 307.1 ATM	
1800	2X(MAX ABSORPTION)X1M=32.4	
1900	RELAXATION FREQUENCY=150.8 KHZ	
2000	(SIGMA)X1M=.23578538	
2100	MAX ABSORPTION RANGE	
2200	15.96 < 16.20 < 16.44	
2300	MAX AB	REL FR SIGMA
2400	16.0	85KHZ .982
2500	16.0	90 .896
2600	16.0	95 .813
2700	16.0	100 .733
2800	16.0	105 .658
2900	16.0	110 .586
3000	16.1	115 .518
3100	16.1	120 .455
3200	16.1	125 .397
3300	16.1	130 .345
3400	16.1	135 .301
3500	16.2	140 .267
3600	16.2	145 .245
3700	16.2	150.8 .236
3800	16.2	155 .240
3900	16.2	160 .256
4000	16.3	165 .280
4100	16.3	170 .308
4200	16.3	175 .340
4300	16.3	180 .374
4400	16.4	185 .409
4500	16.4	190 .443
4600	16.4	195 .478
4700	16.5	200 .511

## HSUDATAW (04/17/81)

100	46.6705,36.410	16.4,1.64
200	57.4076,43.117	23.5,2.0
300	61.0974,48.691	28.0,2.16
400	61.1074,45.292	26.2,2.16
500	76.8504,54.500	39.5,3.12
600	99.9970,59.557	56.6,4.87
700	100.0072,59.551	56.6,4.87
800	111.4101,58.623	63.0,6.27
900	123.6134,58.815	71.4,8.25
1000	133.1556,57.670	76.9,10.2
1100	140.3397,56.932	81.1,11.7
1200	152.2397,61.633	96.5,15.0
1300	171.1000,60.760	111.1,20.8
1400	171.1058,59.412	109.1,20.8
1500	180.0021,58.619	115.4,23.75
1600	180.0354,58.513	115.4,23.75
1700	190.3260,55.923	120.0,27.55
1800	190.5429,57.099	122.5,27.6
1900	205.0760,54.904	130.4,32.6
2000	250.7109,53.635	164.6,48.0
2100	256.1712,52.447	166.7,50.0
2200	271.9823,52.065	178.6,55.6
2300	304.2521,50.554	200.0,66.4
2400	349.8114,46.438	221.0,79.9
2500	0.0	
2600	SEAWATER AT 1 ATM	
2700	2X(MAX ABSORPTION)X1M=122.6	
2800	RELAXATION FREQUENCY=140.3 KHZ	
2900	(SIGMA)X1M=.45766051	
3000	MAX ABSORPTION RANGE	
3100	60.84 < 61.30 < 61.76	
3200	62.3	115KHZ .983
3300	62.0	120 .821
3400	61.8	125 .679
3500	61.6	130 .565
3600	61.4	135 .487
3700	61.3	140.3 .458
3800	61.2	145 .478
3900	61.1	150 .538
4000	61.1	155 .620
4100	61.1	160 .715
4200	61.1	165 .816
4300	61.2	170 .918
4400	61.2	175 1.020
4500	61.3	180 1.121
4600	61.4	185 1.219

## HSUDATAX (04/17/81)

100	46.9989,35.152	16.0,1.65
200	51.1083,39.939	19.5,1.77
300	61.5067,44.399	25.9,2.18
400	65.4441,42.555	26.6,2.41
500	73.6503,45.207	31.8,2.88
600	76.0567,49.423	35.7,3.05
700	78.0177,51.501	38.1,3.2
800	88.9794,54.679	46.2,3.94
900	92.3029,54.157	47.6,4.18
1000	100.3402,55.189	53.0,4.9
1100	102.6307,55.292	54.5,5.21
1200	125.2917,54.122	67.5,8.6
1300	144.7949,54.863	81.6,12.6
1400	156.1754,51.587	86.2,15.22
1500	180.3443,55.762	111.1,23.75
1600	197.7305,53.916	123.1,30.5
1700	201.5357,54.496	127.0,31.6
1800	238.5645,52.264	152.1,43.8
1900	257.8592,46.032	153.8,50.7
2000	275.4739,45.345	165.3,56.8
2100	302.8126,48.361	193.2,66.0
2200	346.5274,45.217	215.1,79.0
2300	0.0,0.0	
2400	SEAWATER AT 71.1 ATM	
2500	2X(MAX ABSORPTION)X1M=115.5	
2600	RELAXATION FREQUENCY=139.9 KHZ	
2700	(SIGMA)X1M=.54319649	
2800	MAX ABSORPTION RANGE	
2900	57.21 < 57.75 < 58.29	
3000	MAX AE	REL FR SIGMA
3100	57.2	110KHZ 1.245
3200	57.2	115 1.065
3300	57.3	120 .901
3400	57.4	125 .759
3500	57.5	130 .643
3600	57.6	135 .568
3700	57.76	139.9 .543
3800	57.9	145 .569
3900	58.0	150 .635
4000	58.2	155 .727
4100	58.3	160 .832
4200	58.5	165 .944
4300	58.6	170 1.059



## HSUDATAY (04/17/21)

100	47.5470,31.817	14.8,1.66
200	51.7037,35.204	17.6,1.79
300	55.0321,36.987	19.6,1.92
400	62.4698,38.997	23.4,2.24
500	65.7776,42.164	26.5,2.41
600	70.3447,41.382	28.0,2.715
700	76.9239,46.643	34.3,3.135
800	80.9002,47.019	36.4,3.36
900	84.5595,47.480	38.5,3.61
1000	89.9395,48.745	42.1,4.02
1100	93.8648,49.306	44.5,4.3
1200	97.8886,50.996	48.0,4.64
1300	104.5171,52.653	53.2,5.4
1400	126.4701,48.957	62.5,6.72
1500	140.0437,49.062	71.4,11.72
1600	150.1304,50.766	80.6,14.4
1700	170.7116,48.705	93.0,20.78
1800	205.5265,47.298	117.6,33.0
1900	225.3791,43.522	125.0,39.8
2000	240.4456,43.284	134.7,44.3
2100	260.1194,40.453	142.9,51.5
2200	275.4892,42.793	159.4,57.0
2300	300.2087,38.119	164.6,65.2
2400	324.9736,39.253	183.5,72.7
2500	350.6535,38.677	198.0,80.2
2600	0.,0.	
2700	SEAWATER AT 168.1 ATM	
2800	2X(MAXIMUM ABSORPTION)X1M=103.8	
2900	RELAXATION FREQUENCY=133.4 KHZ	
3000	(SIGMA)X1M=.34312532	
3100	MAX ABSORPTION RANGE	
3200	51.56 < 51.90 < 52.24	
3300	MAX AB	REL FR SIGMA
3400	51.4	105KHZ 1.021
3500	51.5	110 .852
3600	51.5	115 .694
3700	51.6	120 .552
3800	51.7	125 .434
3900	51.8	130 .359
4000	51.9	133.4 .343
4100	52.0	135 .347
4200	52.1	140 .397
4300	52.2	145 .467
4400	52.3	150 .594
4500	52.5	155 .709

HSUDATAZ (04/17/81)

100	48.1038,28.777	13.7,1.676
200	52.3098,28.578	14.8,1.815
300	62.9993,34.959	21.4,2.27
400	71.1710,37.448	25.9,2.75
500	75.4765,37.508	27.6,3.01
600	85.2856,39.471	32.9,3.66
700	94.4691,43.068	39.7,4.36
800	98.3474,41.323	40.0,4.7
900	105.3827,42.912	44.8,5.52
1000	126.9361,43.535	56.8,8.8
1100	158.4414,44.833	78.4,16.7
1200	183.5608,40.554	89.9,25.1
1300	201.9427,40.962	103.6,31.75
1400	221.0386,40.835	116.6,38.2
1500	246.8549,39.148	130.7,46.75
1600	274.2978,37.901	146.5,56.2
1700	300.1025,37.711	163.3,65.0
1800	329.6653,32.827	168.1,74.1
1900	350.0383,33.482	181.9,80.0
2000	0.0.0.	
2100	SEAWATER AT 307.1 ATM	
2200	2X(MAX ABSORPTION)X1M=90.4	
2300	RELAXATION FREQUENCY=142.1 KHZ	
2400	(SIGMA)X1M=.31661221	
2500	MAX ABSORPTION RANGE	
2600	44.88 < 45.20 < 45.52	
2700	MAX AB	REL FR SIGMA
2800	45.1	110KHZ 1.092
2900	45.1	115 .924
3000	45.1	120 .764
3100	45.1	125 .617
3200	45.1	130 .486
3300	45.2	135 .381
3400	45.2	140 .323
3500	45.2	142.1 .317
3600	45.2	145 .327
3700	45.3	150 .387
3800	45.3	155 .478
3900	45.4	160 .581
4000	45.4	165 .690
4100	45.5	170 .799
4200	45.5	175 .907
4300	45.6	180 1.012

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